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Development and validation of gamma spectrometric analysis procedure using a high purity Germanium detector

Master's Thesis (30 ECTS)

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ABSTRACT

The aim of this study was to develop and validate a gamma spectrometric analysis procedure using a high purity Germanium detector.
The new hardware comes with a new tool which includes a feature that allows standard-free calibration measurements. The calibration software LabSOCS (Laboratory Sourceless Calibration Software) was implemented in the analysis procedure. LabSOCS is based on the geometrical characterisation of the detector for proper efficiency calibration of the system.

During the course of the experiments, it was discovered that the detector in use in the laboratory did not meet the agreed procurement standards, and the supplier had not performed a precise geometrical characterisation of the detector. In order to overcome this drawback, some correction factors were introduced to improve the accuracy of the results.

This paper summarizes the implementation of these correction factors, and also how the analysis procedure addressed the validation parameters using several certified reference materials. The validation parameters included accuracy, precision, detection limit and robustness. The results proved that the analysis procedure is suitable for its intended use with limited expectations, as the activity concentrations of the measured radionuclides were in good agreement with the reference values.

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1 INTRODUCTION

Ionising radiation is present in the environment due to the stream of particles or electromagnetic waves that are emitted by the atoms or nucleus of radioactive substance as a result of nuclear decay. The major contributors include naturally occurring radioactive nuclides (radionuclides) and industrial actions such as the nuclear, coal and mining industries which create an end product that is considered radioactive ‘waste’ product. This waste has elevated radioactivity compared to background levels until now and human exposure to ionising radiation has the potential for harmful effects, such as radiation sicknesses and cancer. When materials contain radionuclides which are highly active, this situation should be controlled, and for this purpose, methods are developed to measure radionuclides in our environment.

Gamma ray spectroscopy is the method used to identify and quantify gamma emitting radionuclides in a variety of matrices. By measuring several gamma rays emitting radionuclides in a sample, the measurement gives a spectrum of lines, and the abscissa represents the activity of the radionuclide, while the ordinate represents its energy (1). Gamma-ray spectrometry is an important technique for characterising radionuclides due to high penetration of gamma rays into the matter being analysed, compared to other forms of analytical techniques (2), and has been well established for many decades in the laboratory as well in the field work. This paper reports on the validation results of a new detection system which allows the possibility to increase the efficiency of measurements. The new hardware comes with a new tool (geometry-based calibration) which includes a feature that allows a standard-free calibration, thus saving time and reducing costs. Implementing this new technique requires careful development and validation of the new standard measurement procedure for the detection system. The analysis procedure needs to be validated to show that it is suitable for its intended use.

2 THEORETICAL BACKGROUND

2.1 PRINCIPLES OF GAMMA RAY SPECTROSCOPY

Nuclear decay takes place typically through the emission of alpha and beta particles. The daughter nucleus produced is usually left in an excited state. After about 10^{-12} seconds (for Cs-137) (this can vary depending on radionuclide), there is the emission of a gamma ray photon that is caused by the relaxation process into a lower energy state. Figure 1 is an example of Cs-137 decay, where 5.4 % of β decay goes directly to the ground state, while 94.6 % goes to an excited nuclear state of Ba-137 and a gamma ray is released before it reaches the ground state. The energy released is 661.7 keV, which serves as the Cs-137 gamma line (3). Gamma spectrometry makes use of this characteristic gamma emission from the nuclear decay process.

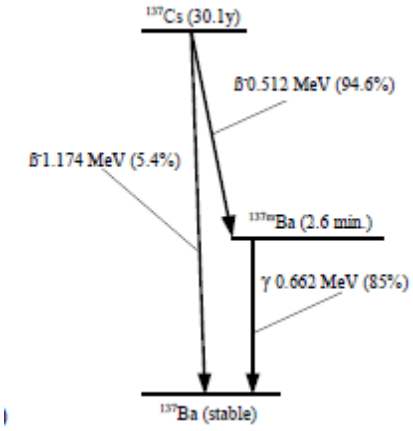

Figure 1: Decay scheme for Cs-137 (4)

2.1.1 Photon interaction with matter

The probability of an interaction to occur depends on the atomic number and density of the element. Each of the interaction processes listed below occurs either by absorption or by scattering away from the direction of the matter which can be characterised by a fixed probability of occurrence per unit length in the absorber. The sum of these probabilities when the gamma-ray photon is absorbed by the nucleus is the probability per unit path length which is called the linear attenuation coefficient as expressed in Equation 1 (5).

$$I = I_0 e^{-\mu_l L} \quad [1]$$

$\mu_l =$ attenuation coefficient (expressed in m^{-1});

I = number of remaining photons in the matter of original intensity;

I_0 = initial intensity;

L= distance

Gamma photons interact with matter through Columbic force, a photon hits an atom and an electron knocks out of the atom causing the atoms to leave the orbitals. During this process, a photon either loses all or part of its energy to the electrons which are as a result of ionisation and excitation of the material atoms. For this kind of radiation the most important mechanism of interactions are:

2.1.1.1 Photoelectric effect: In photoelectric effect, a gamma photon disappears and all its energy is transferred to an electron. Afterwards, assuming that the electron is at rest, it will travel in the same direction (law of momentum conservation) as the gamma photons as shown in Figure 2(a) (6).

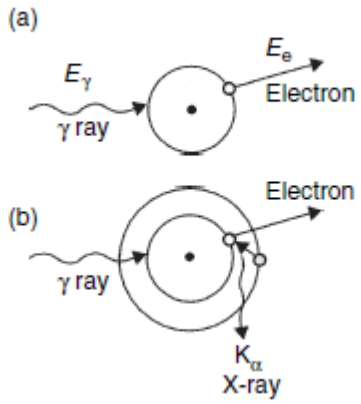

Figure 2: (a) The mechanism for photoelectric absorption (b) emission of electron and fluorescent x-ray (3)

In Figure 2(b), after the ejection of the electron, a higher energy electron fills up the space which results in the emission of the characteristic X-ray which is called X-ray fluorescence. The energetic knock-out electron will continue dissipating the kinetic energy by secondary processes which will result in the release of further electrons which takes place outside the atom in the matter. This interaction is the most useful process in gamma spectrometry because the deposition of all energy in the detector is a precondition for the identification of radionuclides.

2.1.1.2 Compton scattering: Here, the gamma photon loses only part of its energy after it interacts with an electron, and goes in a new direction at lower energy as compared to the photoelectric effect (6). "*The electron gets the remaining energy and is sent out in a direction that conserves the total linear momentum. In a detector, for example, this statistical energy loss from Compton scattering creates a continuous distribution in the energy spectrum"* (6).

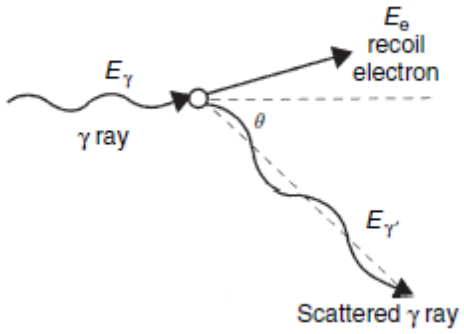

Figure 3: Mechanism for Compton scattering (3)

The relationship between energy of the scattered gamma ray and Compton electron E_e can be expressed as:

$$E_e = E_\gamma - E'_\gamma \quad [2]$$

OR

$$E_e = E_\gamma \left\{1 - \frac{1}{[1 - E_\gamma(1 - cos\theta)/m_0c^2]}\right\} \quad [3]$$

Where,

E'_γ- Energy of the scattered gamma-ray

θ - scattering angle (in the range of $0^\circ$to 180°)

$m_oC^2 = 511.0\ keV$

2.1.1.3 Pair production: This is a phenomenon whereby energy from gamma-ray is converted to mass or matter in the presence of Coloumbic field, as it happens in matter, and not in a vacuum. This occurs with high energy gamma rays, where energy is converted into an electron-positron pair. It can also be termed as the formation of two electrons: a negative and a positive (positron) as shown in Figure 4. Pair production is started when photon with energy (greater than or equals to 1.022 MeV) passes near the electric field of a large atom.

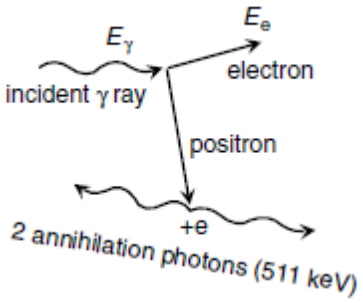

Figure 4: Mechanism for pair production (3)

2.1.2 Summary of interaction process

Compton scattering is mostly important in the mid-energy range while photoelectric interaction occurs at the low energy range and pair production at the high energy range as shown in Figure 5 (3). Each interaction process is a result of a transfer of gamma ray energy to electrons in the gamma ray detector which is the absorbing medium (3). Each of these interactions in the case of the Germanium detector plotted as a function of energy is as shown in Figure 5:

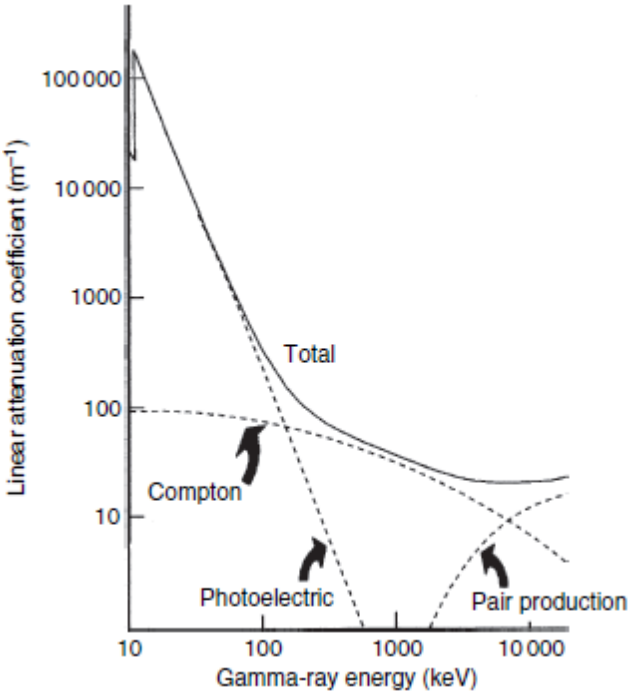

Figure 5: Linear attenuation coefficient of each interaction in Germanium (3)

2.2 GAMMA RAY MEASUREMENT SYSTEMS

The principal interactions described above can take place in any matter. These effects can be utilised as the basis of a detection system. The electrical charges created by the secondary processes in the matter can be collected if an electrical potential is applied to the matter, then amplified and finally transformed into an input of the detector's acquisition system.

In gamma-ray spectrometry, identifying gamma-ray energy is crucial; therefore, the major objective is to convert photon energy into proportional electrical pulses (1). A pulse is produced when the photons emitted from the sample interact with the Germanium crystal. In the detector under electrical tension, the dissipated energy and the pulse height which is also called signal amplitude are proportional to each other as shown in Figure 6 (7). *"The input pulse height (PH) is compared with linearly increasing ramp voltage"* (7).

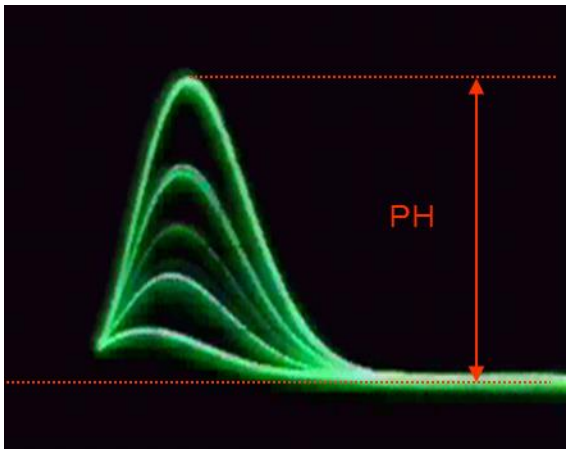

Figure 6: Signal amplitude conversion (7)

Each pulse which is amplified, shaped and sorted as illustrated in Figure 7 in line to pulse height will finally show a histogram. This histogram also called spectrum refers to the counts per unit energy of the incident photons (8).

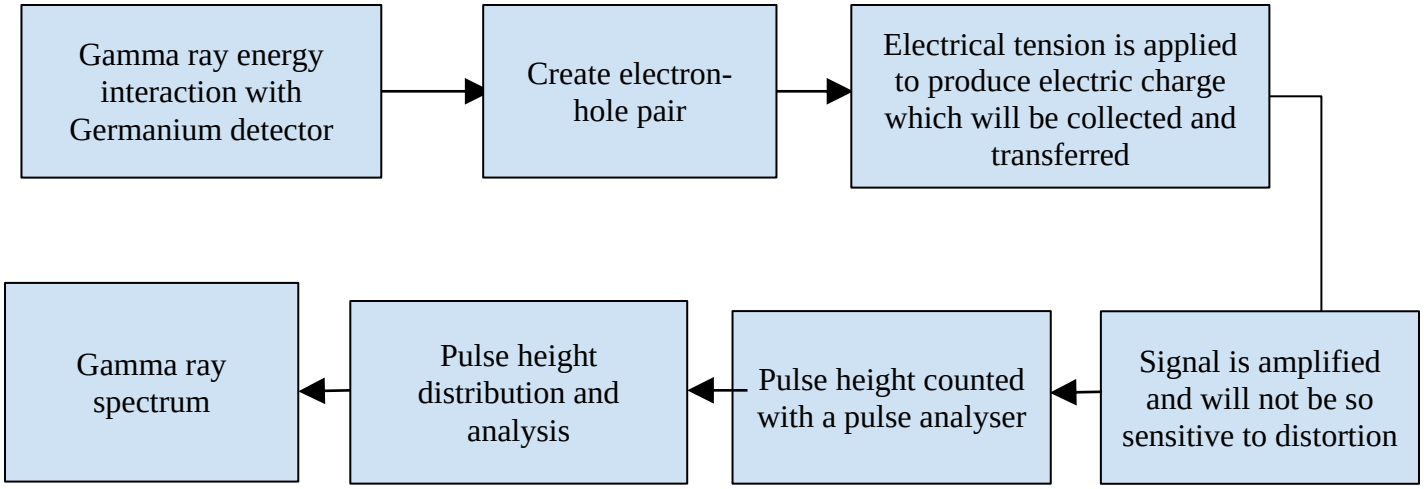

Figure 7: Flow chart showing photon interaction and spectrum formation

A typical high-resolution gamma-ray spectrometry system comprises a mechanical cooling system or liquid nitrogen, the Germanium (Ge) detector, digital signal processing including Multi-Channel Analyser (MCA), and a computer which is the readout device. This is shown below in Figure 8.

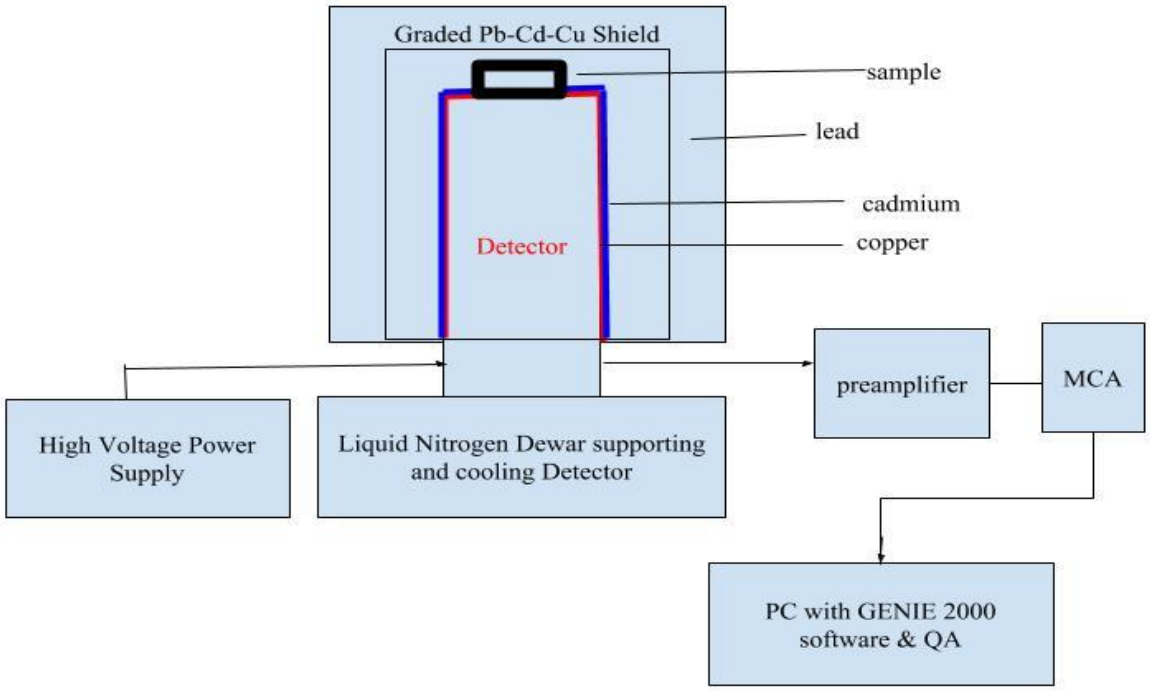

Figure 8: Diagrammatic representation of gamma spectrometer system (9)

2.2.1 Germanium detectors

For the purpose of this work, a Germanium detector was used, to have high-resolution gamma-ray measurement. It is broadly used especially for gamma-ray spectrometry as well as particle detectors.

A typical gamma-ray detector is fabricated from a material which has a relatively low conductivity; therefore, a resistive material is always used (5). It can also be referred to as a total absorption detector for gamma rays because of its sensitivity.

The purpose of a High Purity Germanium (HPGe) detector is to convert gamma rays into electrical impulses which can be processed into signals to determine their energy and intensity. The Germanium detector can either called N-type or P-type. The definition is related to excess charge carriers, depending whether electrons or holes dominate in the germanium crystal and determine the type of electrodes, which serve as electrical contacts to the crystals [24]. N-type detectors are called central n^+ contacts and P-type detectors are called p^+ central contact. The thicknesses of both contacts refer to the dead layer around the crystal surface where energy depositions take place and therefore do not result in detector signals. The central contact and surface contact in these detectors are opposite to each other, whereby the dead layer in the P-type detector is bigger to that of N-type detector (10). Common dead layer thicknesses consist of several hundred micrometres for a Lithium diffusion layer, and a few tenths of a micrometre for a Boron implantation layer. Massive shielding often surrounds the detector, as this helps to reduce the background gamma-ray noise which can be caused by other sources apart from the sample. The shielding consists of Lead which is normally 10 cm thick, and that will absorb a large quantity of background gamma rays (10). Positioning the sample within the shielding is about few distances from the detector. The distance is dependent on the geometry of the sample container.

Before the implementation of a HPGe detector, there could be electron impurities trapped in the crystals which may affect the performance of the detector. After the introduction of a purification technique, the signals produced by the Germanium crystal which has been doped with Lithium ions to create an intrinsic region, and allow the electron-holes to be able to reach the contact surface. HPGe detectors are produced mainly in two types of configurations which include

planar and coaxial as shown in Figure 9 (a) and (b) (10). These refer to how the detectors are wired in the detector circuit and how the crystal is shaped (10). The planar detector crystal consists of either a rectangular, or circular, cross section with a sensitive thickness of 1-20 mm. Based on the gamma-ray energy region that is associated with the area of interest, the thickness of the crystal is chosen based on this (10). Due to the low capacitance of planar detectors, they normally achieve the best energy resolution and are therefore usually preferred for detailed spectroscopy, for example, for the analysis of the complex low-energy gamma-ray and x-ray spectra of Uranium and Plutonium (10).

"Coaxial detectors are produced either with open-ended (the so-called true coaxial) or closed-ended crystals. Coaxial detectors can be produced with large sensitive volumes and therefore with large detection efficiencies at high gamma-ray energies. In addition, the radial electric field geometry makes the coaxial (especially the open-ended coaxial) solid-state detectors best for fast timing applications" (10).

Figure 9: (a)P-type HPGe crystal geometry (b) N-type HPGe crystal geometry (11)

2.2.2 Principles of LabSOCS (Laboratory Sourceless Calibration Software)

LabSOCS is a mathematical computer program used for efficiency calibration and brings a new level of potential to gamma ray measurement without the use of radioactive sources for detector efficiency calibration (12). It allows quick calibrations for various possible geometries. The detector characterisations are produced using Monte Carlo simulation code, physical geometry data of the sample (such as sample material, density, container wall thickness, sample chemical composition and sample filling height) and that of the detector (source to detector distance). The geometry data is defined by the user in the software and this information generates a custom efficiency calibration using Equation 4 for the exact detector and sample as shown in Figure 10 (12). Calibration with LabSOCS can be done in energy range 10-7000 keV.

$$Efficiency\ (E_y) = \frac{Counts\ per\ second\ observed\ in\ the\ spectrum\ photopeak\ (E_y)}{Emitted\ gamma\ rays\ per\ second\ by\ the\ source\ (E_y)} \quad [4]$$

"In general, LabSOCS is accurate to within 4-5 % for energies greater than 400 keV, 7-11 % at 1 standard deviation for energies between 50-400 keV and 20 % for energies less than 50 keV" (12). This was an extensive test by the Canberra Industries (12) using 119 test geometries for LabSOCS and standard calibration which agree within a few percent (12).

These uncertainties are assigned automatically and are calculated into the final result, but uncertainties that are taken into account are not expressed. According to the validation of accuracy of LabSOCS by Bronson, F.L (13) shows that this test is accurate at energies greater than 400 keV and the results obtained using LabSOCS are better than most standard-based calibrations. This was justified by testing eight different detectors created for routine production method (13).

The main drawback of LabSOCS is that it is expensive to acquire and also the need to know the exact composition of the sample material. In case when the exact composition is not known, an assumption need to be made and this may adversely affect the accuracy of the obtained results.

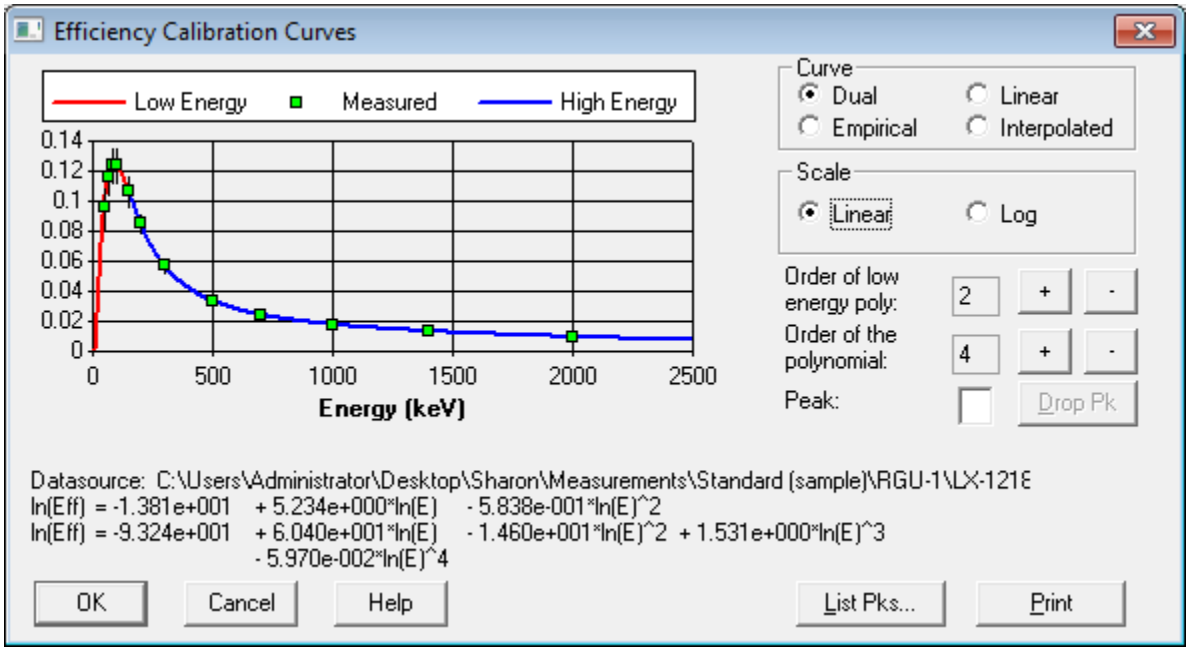

Figure 10: Efficiency calibration curve

2.3 DESCRIPTION OF CANBERRA DETECTOR: n-type 71mm planar BE3830-P

2.3.1 Broad Energy High Purity Germanium Detector (Canberra)

The Broad Energy Germanium detector (BEGe) belongs to a group of HPGe detectors and it was used in current research work. An example of this is the Canberra detector as shown in Figure 11. The detector is of the planar N-type with planar crystal geometry configuration. The Canberra BEGe detector has a unique energy range of 3 keV to 3 MeV which is different from other detectors. It has lower background noises than other typical detectors because it is more transparent to high photon energies. Most low energy detectors are named appropriately because they have a low efficiency at higher energies; in fact, the resolution is not usually specified above 122 keV. The efficiency and energy resolutions of Canberra detectors are optimized in the 3 keV to 662 keV energy regions where the gamma ray of interest lies. The BEGe represents a breakthrough in this respect (12). The crystal offers highest efficiencies for samples counted close to the detector. It has a thin stable entrance window made of carbon epoxy and thickness 0.6 mm, which allows low attenuation and high efficiency for low energy gamma photons in measurement.

The Canberra detector is vertically placed and is protected by a shield predominant material (Lead) and cooled by liquid Nitrogen. This shielding with a thickness of 100 mm is designed to reduce background influence and improve detector capacity to detect in such a way that small low-level samples can also be counted. The Canberra detector also comes with a Lynx digital signal analyser which is capable of the highest quality acquisition and analysis. It is a fast digitizing analogue-to-digital converter (14). In this report, samples were measured with the gamma spectrometer N-type 71mm planar broad energy high purity Germanium detector **(**Canberra) model type BE3830-P as shown in the geometrical illustration as shown in Figure 12.

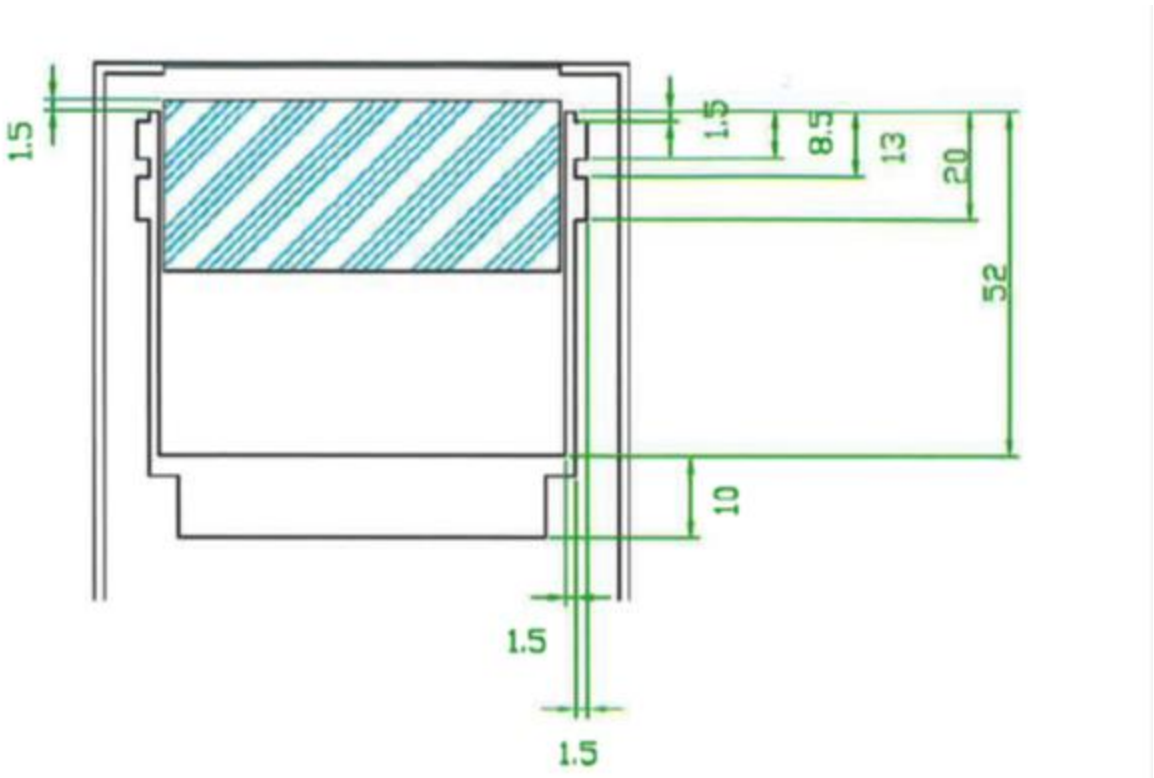

Figure 11: Inner drawing of Canberra crystal model type BE3830-P

Figure 12: Full Canberra detector system with the liquid nitrogen Dewar and lead shielding

2.4 PROCESS OF VALIDATION

Validation is a confirmation by examining and providing evidence that a particular requirement for an analysis procedure meets its intended use (15). It also determines the performance characteristics and limitations of an analysis procedure. A procedure should answer the question of: does the analysis procedure do what it is intended to do?

Validation is determined to be necessary when:

1. A new in-house procedure has been developed,
2. An established method has been reviewed to integrate improvements, or extended to a research new problem (16).
3. A standard procedure is used in another environment, that is, a new laboratory has been created, or a new instrument is used.

In the case of this work, a new in-house procedure was developed, which makes validation necessary.

2.4.1 Validation parameters

- **Accuracy:** This is determined as the closeness of agreement between a measured quantity value and the true quantity value of a measured quantity, which can be expressed as a measurement uncertainty.
- **Trueness:** This is determined as the closeness of agreement between the average of an infinite number of repeated measurements and a reference quantity value.
- **Precision:** This is defined as the closeness and agreement between numbers obtained from the series of measurements of the same sample under the same conditions (17).

It can be expressed as a standard deviation. Precision can be considered at different stages: repeatability, reproducibility or intermediate precision.

1) ***Repeatability:*** This can be defined as a series of measurement carried out on the same (or identical) samples under the same conditions. The standard deviation of the result characterises the repeatability of the measurements, and is also called “within run” precision. Repeatability is denoted by s_r (15).

2) ***Reproducibility:*** This can be defined as a series of measurement carried out on the same (or identical) samples under different conditions, then the standard deviation characterizes reproducibility, and is expressed as s_{RW} (17).

- **Detection limit:** The smallest quantity of analyte in a sample that can be detected in an analysis procedure but might not necessarily be an exact value, is referred to as a detection limit (17).
- **Quantitation limit:** In an analysis procedure, this is the lowest amount of analyte that can be significantly deduced with precision and accuracy, and this particularly important for the determination of impurities (17).
- **Linearity:** An analysis procedure has to be able to give linear test results within a given scope which is directly proportional to the quantity of analyte in the sample (17).
- **Range:** This indicates accuracy, precision, and linearity of an analysis procedure, and is the distance between upper and lower amounts of analyte in a sample (17).
- **Robustness:** This has to do with the ability of an analysis procedure to remain unchanged either by small, or deliberate variation in various parameters, and thus shows that it is reliable for use (17).

2.4.2 Tools for validation

In order to carry out validation, the following tools are used:

- Validated modelling tools;
- Certified reference materials;
- Interlaboratory comparisons;
- Blank samples;
- Repeated measurements.

2.4.3 Parameters selected for validation

The accuracy of the analysis procedure was checked by comparing the laboratory result with reference value with use of some formulas as shown in Equation 19.

Robustness was carried out by checking how the efficiency of LabSOCS can be affected by comparing variations of chemical compositions.

Precision was checked by using quality assurance in Genie to see the variations in activity concentrations of radionuclides over periods of time. Also, background measurements were checked in case of low activity samples, since variations in background influence precision. The relative standard deviation was compared with the pooled standard uncertainty of certain radionuclides.

Detection limit for certain radionuclides was listed which could vary at different conditions and this was explained more in Chapter 4.

The tool used for validating the analysis procedure in this report was a validated modelling tool which was used to calculate self-attenuation and correction factors, blank samples, samples analysed with repeated measurements for precision estimation and background variation and certified reference materials which are discussed in Chapter 3.

3 ANALYSIS PROCEDURES AND MEASUREMENT

The analysis procedure is aiming at measuring any gamma ray emitting radionuclides using gamma spectrometry with an energy range of 40-2000 keV. This chapter describes the gamma spectrometric measurement and spectrum analysis.

3.1 SAMPLE TYPE AND GEOMETRY

Measurements are carried out on the gamma spectra of natural radionuclides in different environmental samples which included hay and sand. Firstly, they were dried in the oven and put in a desiccator to cool down. Samples were prepared in a pre-defined geometry of 57 cm^3 cylinder beaker, with fixed diameter of 6.09 cm, and height of 1.91 cm. Samples in this geometry were compacted in a metallic beaker, and properly distributed to assure homogeneity. Secondly, another geometry used for measurement was the aluminium cylindrical can (Al+5g of epoxy glue) with geometry of 6.11 cm diameter and 3.70 cm height. For the aluminium can, 5 g of epoxy glue was added to the sample. After the glue was mixed with the sample into a homogenous mass, it was left to dry for at least 2 hours (18). Then the containers are tightly sealed (with this, loss of Rn-222 is minimal during measurement) and ensuring identical measurement geometry. The third geometry used was a “Williams” beaker (this beaker is made of Plexiglas) with a diameter of 4.22 cm and a height of 2.94 cm.

In order to ensure well-fixed sample position, for each geometry, samples were placed in a ring-like material before it was placed on the detector as illustrated in Figure 13: MET57 and Williams Sample holder; this allows the sample to be properly placed on the detector.

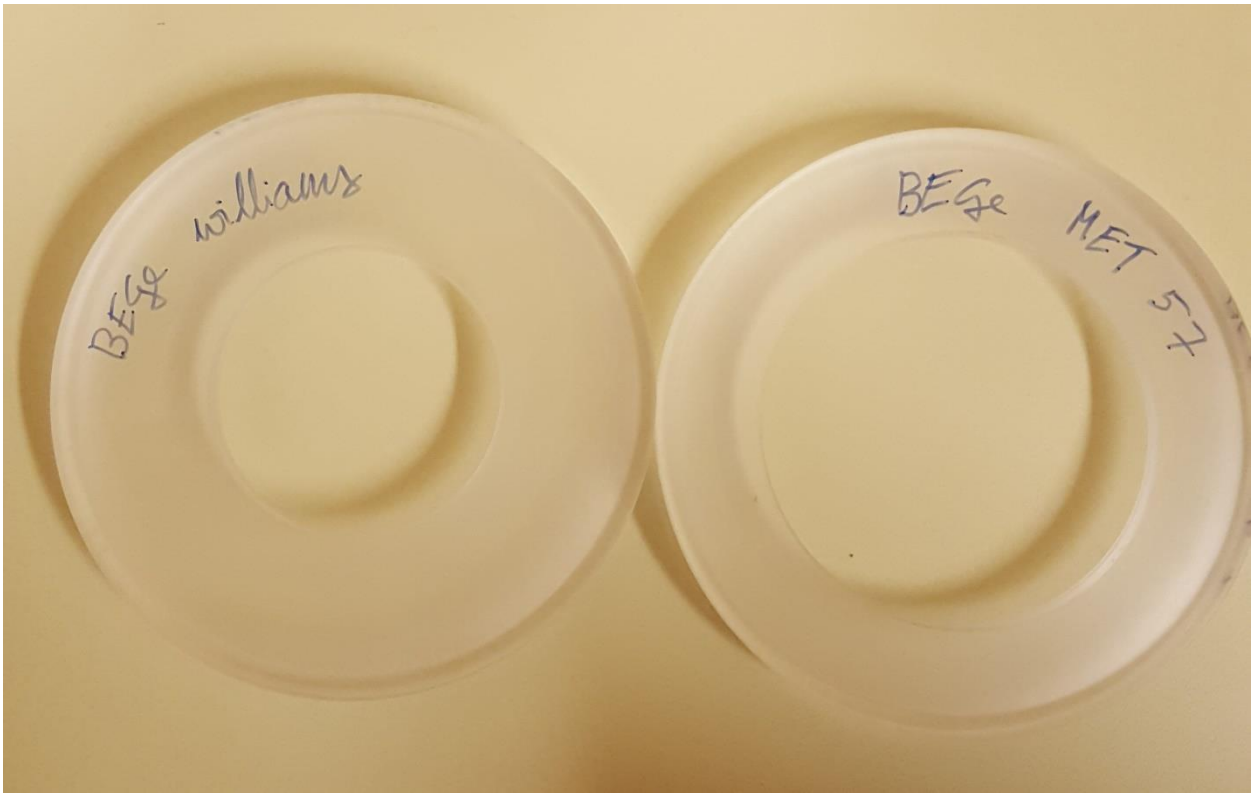

Figure 13: MET57 and Williams Sample holder

3.2 PROCEDURE DESCRIPTION

After the spectra are collected as explained in Chapter 2; we are interested in determining the activity concentration of these radionuclides. *Activity concentration can be referred to as the amount of radioactivity per unit volume and unit mass in materials that include radionuclides* (19).

In order to calculate activity concentration of a radionuclide, basic steps are needed to have a final result with the assistance of a software package; Genie 2000 gamma analysis software (version 3.3) as shown in Figure 14.

The main steps for undergoing this analysis procedure include: efficiency of the detector which will be done by LabSOCS, energy and peak width calibration (expressed as full width at half maximum (FWHM) of full energy peak), determination of net peak area and determination of background count rate, setting up a nuclear database (nuclide library) with nuclear data required to identify and transform count rates into activity concentrations and their uncertainties.

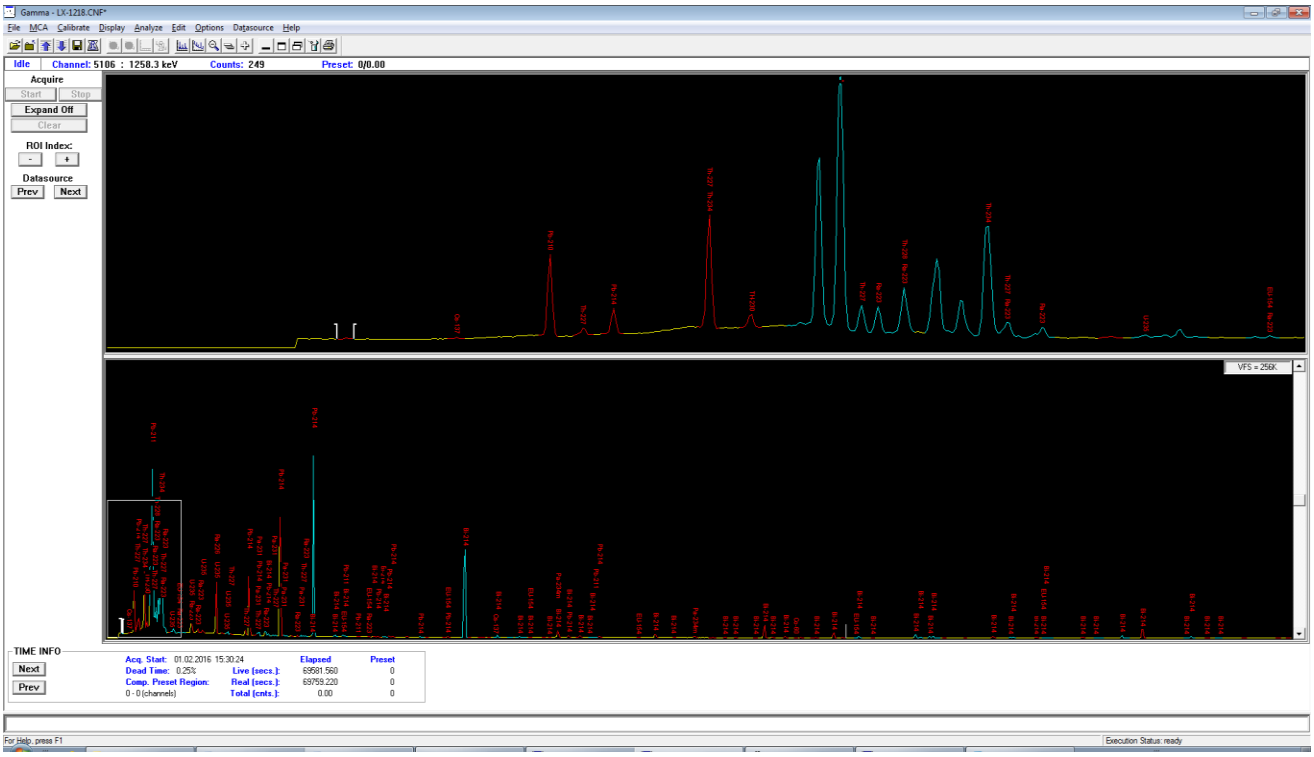

Figure 14: Result Interface from Genie 2000 gamma analysis software presenting the histogram (spectrum) and identified radionuclides

The activities that were involved during spectra analysis by the Genie 2000 software are as described below:

1. Two spectra are required for analysis: one for the sample and one for the background with the empty detector.
2. The user has to define a list of nuclides of interest to Genie 2000. This is referred to as the nuclide library, and it nuclide library contains a list of radionuclides to be analysed with their half-lives and decay intensities of different radionuclides. This database will be used to identify unknown peaks in the sample spectra.
3. The analysis began with creating calibration files which will contain calibration functions for energy and efficiency. Firstly, the energy calibration can be done in either of 2 ways:
   - Recalling the previously saved calibration, or
   - Identifying the peaks manually, based on knowledge of what radionuclides are present in the measured sample.

When either of these steps is selected, we are able to find out what energy corresponds to which specific channel in the spectrum. Then the relationship between the energy and the channel should generate a linear graph by the software.

4. Secondly, the efficiency calibration was done using LabSOCS, which was used to create the efficiency points from energies between 40-2500 keV. Data attributes provided in LabSOCS to calculate the efficiency curve included: the detector geometry, the sample geometry, the chemical composition of the sample with percentage weight, the density of the sample and the distance between sample and the detector. We are able to see how many counts are produced by a radionuclide in the spectrum as illustrated in Figure 10. The self-attenuation coefficient is then taken into account by LabSOCS during the calibration process.
5. Thirdly, a background correction file was created. The main purpose of subtracting background was to remove background peaks from the sample spectrum. The background spectrum refers to the radioactivity coming from anywhere else and not from the sample. The spectrum obtained from the blank sample measurement was analysed by locating the peaks and calculating the peak areas.
6. After completing the above steps, the sample spectrum analysis was performed. The spectrum analysis involved some steps which are explained with the bullet points below. The efficiency calibration file was recalled under the menu “calibrate” - “efficiency”- “by LabSOCS” curve as shown in Figure 10.

- **Peak locate:** This was used to locate the peak of interest. The generalised 2nd order differentiation algorithm was used to locate the peaks which are above the continuum and it automatically identifies the centroids of the peaks in the spectrum. The search region was set to the beginning and end of the channel with a significance threshold of 3.0, (the lower the significance limits the more the sensitivity of locating peaks) as the tolerance level. Based on experience, it is shown that the threshold values lower than 3.00 produce false peaks (20).
- **Peak area:** *“This method automatically finds the region of interest around each peak found by the peak locate method in use”* (20). The net peak area of all the peak multiplets

and singlets were calculated using the fitting method. The sum/non-linear least squares fit peak area was used to calculate the peak area. The set region was set to the start and end of the channel. In the channel box, the FWHM (full width at half maximum) button was selected so that the continuum channel is added as a function of each peak's FWHM. The continuum function was set to a linear function.

- **Area correction:** Here, the net peak area was corrected before further calculations were done. This was done by recalling the background file so that the peak areas which match that of the peak in the sample spectrum will be deleted. A tolerance value of 2.0 was defined to show how large can be allowed, between the peak of the sample spectrum, and that of the background spectrum for it to be considered as the same peak.
- **Efficiency correction:** The respective peak efficiency and its uncertainty values as defined in Equation 12 were automatically calculated by the software (13).
- **Nuclide Identification (NID):** The method used for nuclide identification included interference correction. The nuclide libraries which contained gamma-ray emitting radionuclides, as well as their half-lives and intensities were used to identify unknown peaks in the sample spectra. The nuclides were assigned to each peak they represent and activity was calculated using Equation 4. Several peaks were also used to identify one radionuclide. For example Pb-214 with peaks 242, 295.22 and 351.93 keV. And the mean of the activity of each peak was reported, and also calculated in Becquerel (Bq) with the various uncertainties of each nuclide.
- **Detection limits:** The Minimum Detectable Activity (MDA) values of all nuclides were calculated with a confidence factor of 5%. For finding the minimum detection limit, Currie MDA (Equation 13) was used.
- **Quality assurance analysis (QA):** The QA analysis was used to check the performance of system parameters which was monitored over a period of time. The QA check is done in parallel with measurements. The main parameters checked during measurement included: activity concentration (Bq/g), peak centroid (ch), background, efficiency and full width at half maximum (FWHM). In Figure 15, there is an example, which shows the peak centroid of Bi-214 with an energy line of 351.9 keV for different spectrum analysis. It was seen from the graph that the results were within an acceptable region, as none of

the centroids go beyond the warning (red) line. The horizontal lines are indicated as follows:

i. Accepted limit (black, dot-and-dashed lines) mean $\pm 1\sigma$(limits calculated in such way that the upper and lower limits are addition and subtraction of the mean and once the standard deviation),

ii. Warning line (blue, long dashed lines) mean $\pm 2\sigma$ (limits calculated in such way that the upper and lower limits are addition and subtraction of the mean and twice the standard deviation), and

iii. Action line (red, dotted lines) mean $\pm 3\sigma$ (limits calculated in such way that the upper and lower limits are addition and subtraction of the mean and triple the standard deviation) respectively.

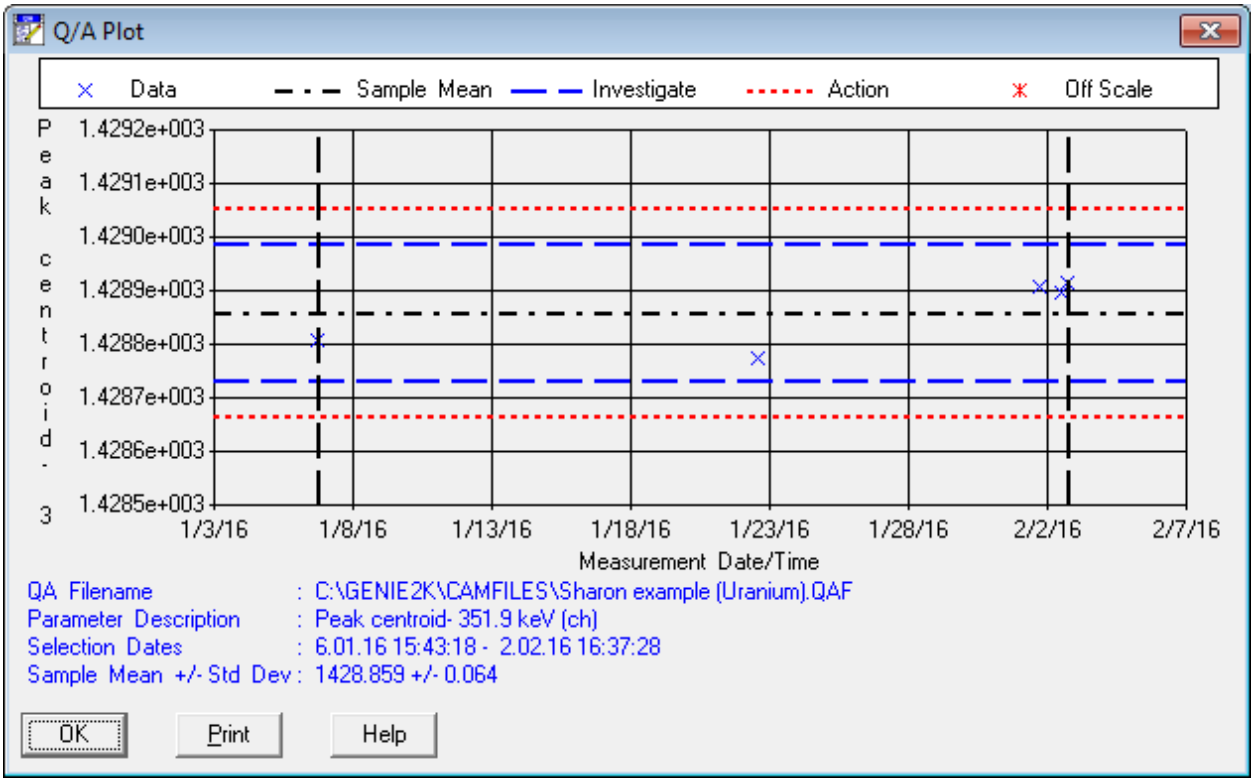

Figure 15: Viewing a QA chart

Finally, the report is generated based on the steps above. Genie 2000 displays the measurement result in a text file (spectrum filename with an extension of .RPT) (20), which include the following information:

1. Description of sample
2. Acquisition data
3. Calibration data
4. Library file
5. Analysis parameters
6. Interference corrected data
7. Unidentified peak
8. Nuclide identification
9. Nuclide MDA
10. Summary of the nuclide library use
11. Summary of the nuclides in the sample with respective activity concentration and their uncertainties

The activity concentration of each radionuclide was expressed in this form:

$$A = \frac{S}{\varepsilon' \times V \times y \times T_1 \times K_c \times K_w \times K_u} \quad [5]$$

where,

S= net peak area;

ε' = attenuated corrected efficiency; i.e, $\varepsilon' = \varepsilon \times^{e^{-\mu(E)\rho t}}$

where;

$\varepsilon = \varepsilon'$ if no attenuation correction is performed;

$\mu(E)$ = mass attenuation (in units of cm^2/g) at gamma energy E; and

ρt = average sample mass per unit area,

V = sample volume (or mass);

y =intensity/branching ratio of peak area;

T_1 =live time of the collect in seconds ;

K_c =correction factor for the nuclide to decay during counting;

K_w =correction factor for the nuclide decay from the time the sample was obtained to the collection time; and

K_u = coincidence summing correction

3.2.1 Analysis Sequence

To avoid running through all these steps on every sample measurement, an analysis sequence command was used in Genie 2000 to create, or edit the analysis sequences that can be used to analyse the spectra automatically. All the procedure parameters listed above in this chapter are already saved in the software, so that it runs through each repetition by itself, instead of a self-input on every measurement. This can be used for subsequent measurements as this procedure has been validated.

3.2.2 Correction coefficients

Correction factors are taken into account during the spectrum analysis.

K_c is the correction factor for the radionuclide to decay during counting.

$$K_c = \frac{T_{1/2}}{ln(2)t_c}\left[1 - e^{-\frac{\ln(2)t_c}{T_{1/2}}}\right] \quad [6]$$

where,

t_c =time during measurement acquisition;

$T_{1/2}$ =half-life of the nuclide

K_w is the decay correction coefficient which takes into account the time the sample was obtained and measurement time. This can be obtained by Equation 7.

$$K_w = e^{(-\frac{\ln(2)t_w}{T_{\frac{1}{2}}})} \quad [7]$$

where,

t_w =elapsed clock time from the time the sample was taken to the acquisition start time (in the same time units as $T_{1/2}$in seconds).

Coincidence summing correction or cascade summing effect is taken into account by Genie. Coincidence summing may happen when two subsequent photons of different energies from the same decay event are detected at the same time by the system. A good example is Co-60 as shown in Figure 16 which deposits energy in the detector at the same time and both gamma events are summed up as one. Summing effect depends on detection solid angle that is, related to source distance to detector geometry. When the sample is far from the detector, the coincidence

summing is low and thereby negligible. But if the sample is directly on the detector, just like the detector used for this measurement, coincidence summing effect has to be taken into account.

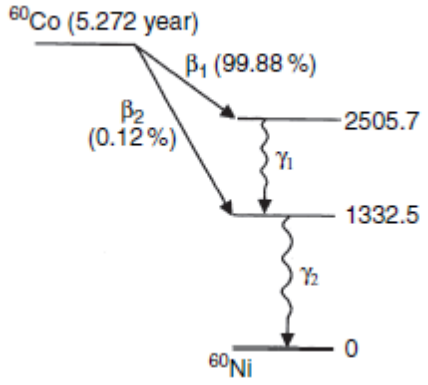

Figure 16: Decay scheme of Co-60 (3)

Genie has made a comprehensive coincidence summing library that contains the source-detector geometry information and is supplemented by nuclear data calculated and based on known theoretical models (21).

In addition, the self-attenuation, or the self-absorption correction coefficient, is also taken into account by Genie in the final result of the calculating activity concentration. This is used to correct attenuation of gamma rays as they propagate in samples and insensitive parts of the detector, which reduces detection efficiency. It depends on densities and chemical composition where photon propagates as described in the attenuated corrected efficiency (22). The Monte-Carlo simulations have been developed in the software for calculating the corrected efficiency detected for any sample, with the help of the known chemical composition (22).

3.3 METHODS TO CALCULATE EFFICIENCY

3.3.1 LabSOCS Correction

There are 2 types of detector characterizations available by Canberra. One is the generic and the second is detector specific. The generic detector characterizations are the detector types which are already modelled in LabSOCS as shown in Figure 17:

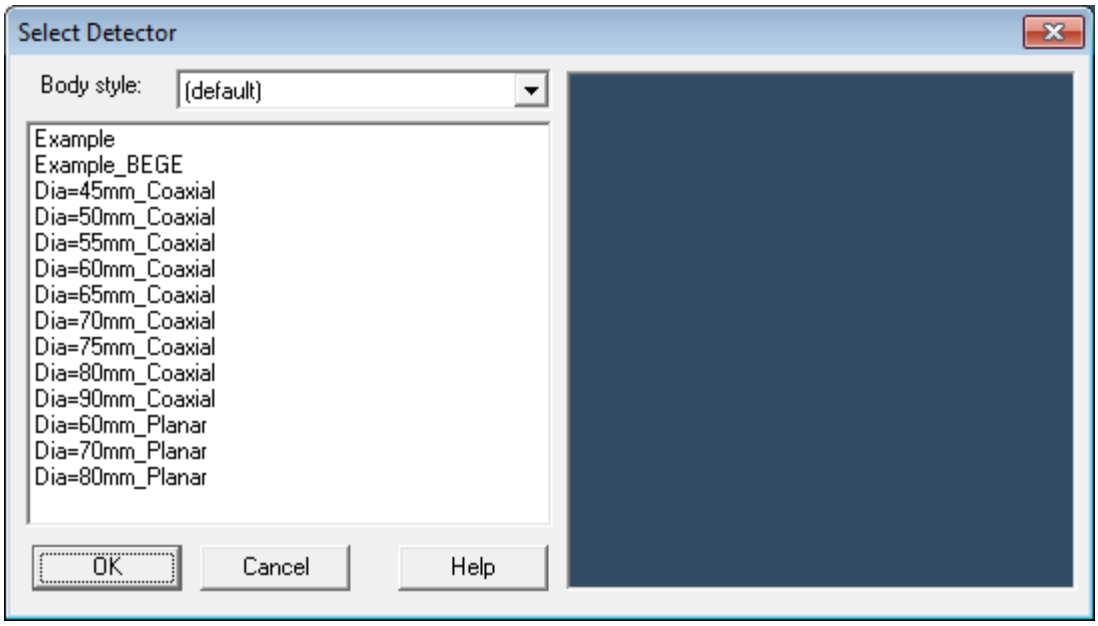

Figure 17: Detector type in LabSOCS

While the detector specific characterization needs a geometrical and technical characterisation of the specific detector in use. The detector specific characterisations give more accurate results when compared to the generic detector characterisations.

The detector specified in LabSOCS which has the closest geometry to the laboratory detector is the 70 mm planar BE3825 with thickness of 25 mm and crystal diameter of 70 mm, while the laboratory detector is the 71 mm planar BE3830-P with thickness 30 mm and crystal diameter of 71 mm. Therefore, since we know that the efficiency is dependent on the detector-sample geometry and the volume of the detector, the efficiency calibration done for measurements in LabSOCS is not for the laboratory specific detector. Because the detector was not characterised by the supplier.

In order to validate the accuracy of LabSOCS, a comparison was done using standard calibration which included the use of EFFTRAN (23) for self-attenuation correction and coincidence summing correction with LabSOCS calibration as discussed below.

3.3.2 EFFTRAN Efficiency Transfer Method

EFFTRAN method of efficiency transfer was needed to validate results of Genie. EFFTRAN is a mathematical model used to perform the efficiency transfer for different chemical composition

and geometry (23). It was used to do the efficiency transfer considering material self-attenuation, geometrical differences between standard and sample, as well as taking into account coincidence summing corrections (24). A calibration standard made from certified reference materials was used for efficiency calculation. A certificate generated from the standard consists of activity concentrations of its daughter radionuclides, the activity concentration in Bq/g and their uncertainties. The certificate was corrected in EFFTRAN for coincidence summing effect. This corrected standard certificate in EFFTRAN was used in Genie to build an efficiency curve. The efficiency curve that was created was then corrected for self-attenuation (using geometry, matrix, and the density of the standard and sample) in the efficiency transfer in EFFTRAN. The efficiency transfer was built for calculating full energy peak efficiencies of the measured sample from the known activities of the reference standard (23). The generated efficiency curve was then used to compare for the LabSOCS efficiency as explained in section 4.1.

3.4 UNCERTAINTY MEASUREMENT

All uncertainty sources are developed in the software as algorithms which calculate the uncertainties automatically. According to the Genie 2000 gamma software analysis software, the combined standard was calculated and represented by Equation 8:

$$\sigma_c = A \times \sqrt{\left(\frac{\sigma_R}{100}\right)^2 + \left(\frac{\sigma_S}{S}\right)^2 + \left(\frac{\sigma_V}{V}\right)^2 + \left(\frac{\sigma_{\varepsilon'}}{\varepsilon'}\right)^2 + \left(\frac{\sigma_y}{y}\right)^2 + \left(\frac{\sigma_K}{K}\right)^2} \quad [8]$$

where,

σ_R =user defined random uncertainty as a percentage;

σ_S =uncertainty of net peak area S;

σ_V = uncertainty of sample quantity V;

σ_y =uncertainty of the branching ratio that is intensity;

σ_K =uncertainty of the composite decay correction factor K;

$$K = K_c \times K_w$$

the uncertainty of decay correction factor, K_w:

$$\sigma_{K_w} = \frac{K_w \times ln(2) \times t_w}{(T1/2)^2} \times \sigma_{T_{1/2}} \quad [9]$$

the uncertainty of decay correction factor, K_c:

$$\sigma_{K_c} = \left| K_c - \frac{t_c \ln(2)}{T_{1/2}} \right| \times \frac{\sigma_{T_{1/2}}}{T_{1/2}} \quad [10]$$

therefore,

$$\sigma_K = K \times \sqrt{\left(\frac{\sigma_{K_c}}{\sigma_{K_c}}\right)^2 + \left(\frac{\sigma_{K_w}}{\sigma_{K_w}}\right)^2} \quad [11]$$

$\sigma_{\varepsilon'=}$ uncertainty of the effective efficiency, which is defined as:

$$\sigma_{\varepsilon'=} = \varepsilon' \times \sqrt{\left(\frac{\sigma_\varepsilon}{\varepsilon}\right)^2 + \left(\rho t \times \sigma_{\mu(E)}\right)^2 + \left(\mu(E) \times \sigma_{\rho t}\right)^2} \quad [12]$$

where,

ε =the non-attenuation corrected detection efficiency at the peak energy;

σ_ε = its uncertainty;

$\mu(E)$ =mass attenuation at gamma energy;

$\sigma_{\mu(E)}$ =its uncertainty;

$\rho\iota$ =average sample mass per unit area;

$\sigma_{\rho\iota}$ =its uncertainty

And lastly, the total uncertainty of the activity, A, is calculated as:

$$\sigma_{C(T)} = \sigma_C + \frac{\sigma_{sys}}{100} \quad [13]$$

where σ_{sys} is the user defined systematic uncertainty as a percentage.

3.5 MINIMUM DETECTABLE ACTIVITY (MDA)

This can be described as the measure of how low an activity could be detected and measured by the analysis. MDA was calculated for unidentified and identified nuclides. There are different ways of calculating MDA but the method used in Genie is based on the Currie deviation as represented in Equation 14:

$$MDA = \frac{L_D}{T_1 \times \varepsilon' \times y \times V \times K_w \times K_c} \quad [14]$$

where,

L_D =detection limit;

T_1 =collection live time in seconds;

ε' =non-attenuation of gamma energy (E); $\varepsilon' = \varepsilon$ if no attenuation correction is performed;

y= branching ratio or intensity of the gamma energy;

V= mass or volume of the sample;

K_c =correction factor due to counting shown in equation 6

K_w =correction factor for the nuclide decay during the time sample was obtained and acquisition start time as shown in Equation 7.

$$L_D = k^2 + 2L_C \quad [15]$$

$$L_C = k \times \sqrt{B + \left(\frac{T_s}{T_b}\right) I_b + \left(\frac{N}{2n}\right)^2 (B_1 + B_2) + \left(\frac{T_s}{T_b}\right)^2 {\sigma_{I_b}}^2} \quad [16]$$

where,

k = the confidence level of 1.645 at 95 %

B = value of the continuum subtracted;

I_b =net peak area of background measurement;

T_s =live time of sample measurement;

T_b =live time of background measurement;

N= number of channels in the peak region of interest;

n= number of channels on each side of the peak region used for the determination of the continuum of counts;

B_1 =sum of counts in the n channels to the left of the peak region;

B_2 =sum of the counts in the n channels to the right of the peak region;

σ_{I_b} =uncertainty of the net peak area of background peak

3.6 STANDARDS FOR VALIDATION

Certified reference materials (Thorium, Uranium, and Potassium) were used for method validation. The Uranium standard (RGU-1) certificate (International Atomic Energy Agency) IAEA/RL/148; manufactured by Canada Centre for Mineral and Energy Technology (CANMET) on the order of IAEA, contains sand (SiO_2) with a known content of Uranium. Reference activity concentration value for Uranium standard is (4.939 +/- 0.025) Bq/g, 95 % k=2 confidence level and the daughter radionuclides are all assumed to be in secular equilibrium.

The Thorium standard (RGTh-1) certificate IAEA/RL/148; manufactured by (CANMET) on the order of IAEA contains sand with a known content of thorium. The activity concentration of the daughter radionuclides of Thorium decay series are in secular equilibrium.
The Potassium standard (RGK-1) certificate IAEA/RL/148; manufactured by (CANMET) on the order of IAEA contains 96 % known content of Potassium which can be identified by its own energy line 1460.83 keV.
Reference materials RGU-1, RGTh-1, and RGK-1 with a reference date of 1st January, 1987 according to the certificate were used for this analysis. The date of 19th May, 2014 as the sealing date of the standards, was input as the reference date for measurements.

Also, the hay sample from proficiency testing 302-IAEA-TEL-2012-03 was used for validation which consists of carbon, hydrogen and oxygen. Since we lack exact information about chemical composition, the representative chemical composition was assessed based on general information available on organic matter. The reference activity concentration for the hay sample for Cs-134 (0.0821$\pm$0.0052) Bq/g and Cs-137 (0.743$\pm$0.0219) Bq/g, 95 % k=2 confidence level. The reference values presented for the hay sample are activity concentration values after the decay of the sample from the reference date on the certificate (1st January, 2012) to spectrum collection date (6th January, 2016).

4 DISCUSSION AND RESULTS

Standard samples were analysed using Genie 2000 analysis software. Standard samples (RGU-1, RGTh-1, and RGK-1) and hay sample were measured for approximately 24 hours. All standard samples were prepared in the same size container 57 cm^3 to get same counting geometry.

4.1 VALIDATING LABSOCS FOR EFFICIENCY

Figure 18 below shows the relative bias between LabSOCS and EFFTRAN efficiencies of 8 different samples with the same geometry which overlap each other except an ash sample in a different geometry (Williams beaker). This means that the deviation is geometry and energy dependent. The relative bias was plotted against the energy as shown in Figure 18. To this effect, correction is made for LabSOCS efficiency, for a particular geometry (met57).

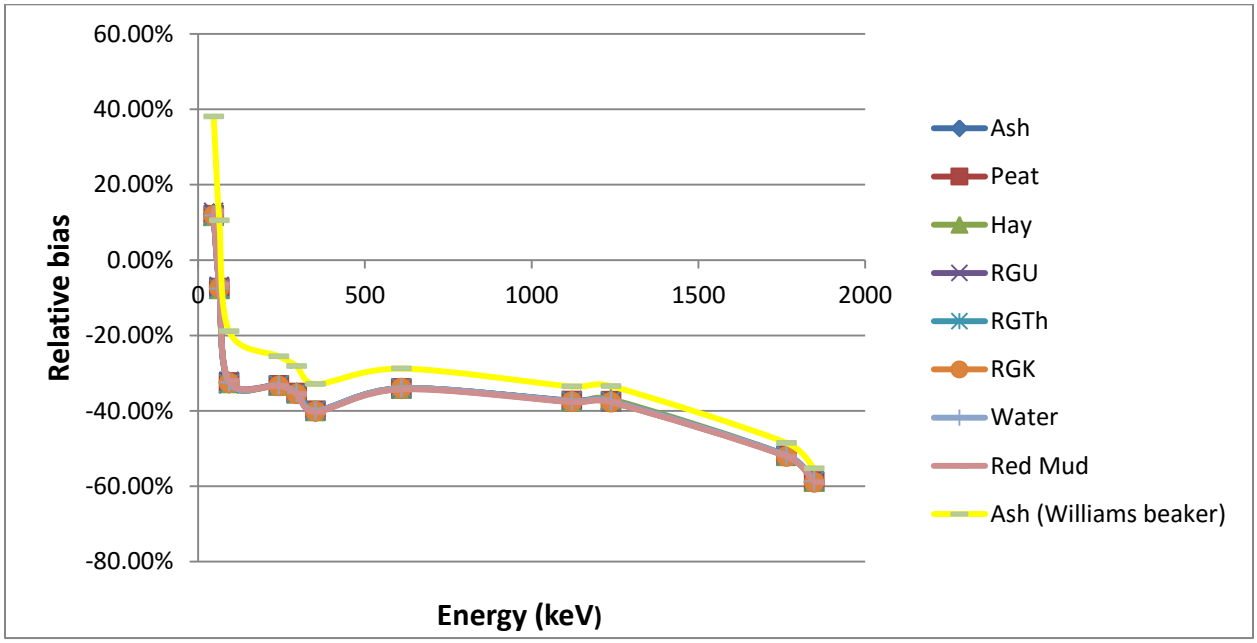

Figure 18: Graph of relative bias against energy of samples in a geometry (met57) and a different geometry (Williams beaker) containing an ash sample (comparing between LabSOCS and EFFTRAN efficiency)

To solve the difference in this efficiency calibration which will improve accuracy, a correction term was introduced. As shown in Equation 17:

$$Correction\ term = \frac{EFFTRAN\ efficiency}{LabSOCS\ efficiency} \quad [17]$$

In order to introduce this correction term, a modification was made to Equation 5. One way to incorporate this correction term was to consider modifying one of the energy dependent parameters: the net peak area, the intensity, or the efficiency. Since the only parameter that could be modified was the intensity, as it is stored outside the Genie software in a nuclide library. A new library was then created for every geometry used that will include these correction terms. Therefore, the Equation 5 was remodelled to become Equation 18:

$$A = \frac{S}{\varepsilon' \times V \times y \times T_1 \times K_c \times K_w \times K_u \times K_a} \quad [18]$$

where all parameters remain the same; and

K_a =LabSOCS correction value

During this experiment, the setback of LabSOCS in the question of accuracy was noticed, and the supplier was contacted in respect to this matter. Now the supplier is working on this problem, and the laboratory will eventually have the exact detector characterisations included in the LabSOCS software. When this is done, there will be no need for a correction factor, and then the usual nuclide library can be used for analysis. This will also avoid the additional uncertainty which is accompanied with the correction factor.

4.2 ACCURACY

The hay sample from the proficiency test, along with the Uranium, and Thorium standard samples were used to check the accuracy of the analysis procedure. Firstly, the accuracy was used to check for sample geometry met 57 as reported in Table 1-Table 3. The accuracy of the method was determined based on E-normal (E_n-value) between laboratory values and certified reference values, as shown in Equation 19. The E_n value was used to evaluate the compatibility of the results. The estimated uncertainty was presented within 95% confidence level, in order to use the En-value formula given below:

$$E_n = \frac{\bar{X}_{lab} - u_{CRM}}{\sqrt{Unc_{CRM}{}^2 + Unc_{lab}{}^2}} \quad [19]$$

where $\bar{X}_{lab}$ is the mean value from measurement

u_{CRM} = certified value

Unc_{CRM} and Unc_{lab} =expanded uncertainty of certified value and laboratory value respectively.

Interpretation of En values:

- | En | ≤ 1: experimental values is consistent with reference value;
- | En | > 1: experimental values is NOT consistent with reference value

Radionuclide	Reference value (Bq/g)	Uncertainty (Bq/g) k=2	Lab value (Bq/g)	Uncertainty (Bq/g) k=1	Expanded uncertainty at k=2 (Bq/g)	E_n value
Cs-134	0.0821	0.0052	0.0821	0.0042	0.0084	**0.195**
Cs-137	0.743	0.0219	0.751	0.040	0.080	**0.301**

Table 1: En value calculation results for the hay sample (met 57)

Radionuclide	Reference value (Bq/g)	Uncertainty (Bq/g) k=2	Lab value (Bq/g)	Uncertainty (Bq/g) k=1	Expanded uncertainty at k=2 (Bq/g)	E_n value
Bi-214	4.939	0.025	4.874	0.105	0.210	**0.307**
Pb-214	4.939	0.025	5.046	0.176	0.352	**0.303**
Pb-210	4.939	0.025	4.661	0.701	1.402	**0.198**
Th-234	4.939	0.025	4.915	0.503	1.006	**0.023**

Table 2: En value calculation results for the Uranium standard (met 57)

Radionuclide	Reference value (Bq/g)	Uncertainty (Bq/g) k=2	Lab value (Bq/g)	Uncertainty (Bq/g) k=1	Expanded uncertainty at k=2 (Bq/g)	E_n value
Ac-228	3.246	0.065	3.128	0.121	0.242	**0.471**
Pb-212	3.246	0.065	3.161	0.256	0.512	**0.165**
Tl-208	1.169	0.065	1.085	0.041	0.084	**0.787**
Ra-224	3.246	0.065	3.020	0.254	0.508	**0.441**

Table 3: En value calculation results for the Thorium standard (met 57)

From the | E_n | values in the above tables, it can be concluded that the results produced by the analysis procedure are correct, and therefore comparable to the proficiency test values obtained by the expert laboratories.

Also, the accuracy of the analysis procedure was also estimated as shown in Table 4 using the z-score in equation 20:

Z-score is calculated as:

$$z = \frac{x_{lab} - x_{ref}}{\sigma} \quad [20]$$

Where,

x_{lab} = laboratory result;

x_{ref} = reference value;

σ = standard deviation of laboratory results.

Interpretation of z-score:

- z<2, the quality of the measurement is satisfactory,
- 2<z<3, the quality of the measurement is questionable,
- z>3, the quality of measurement is poor thus require further analysis.

Radionuclide	Reference value (Bq/g)	Lab value (Bq/g)		Standard deviation	z-score
		Reading 1	Reading 2		
Cs-134	0.0821 ±0.0052	0.081±0.0083	0.084±0.0084	0.002	**0.52**
Cs-137	0.743±0.0219	0.751±0.0874	0.770±0.0892	0.013	**0.61**

Table 4: Z-score calculation results for the hay sample (met 57)

The calculated z-score with values of 0.52 for Cs-134 and 0.61 for Cs-137 indicates that the measurement carried out with the hay sample is at the satisfactory level.

To justify the procedure as being accurate, since a correction factor was introduced in LabSOCS for a specific geometry, it was necessary in the analysis to do a test using Uranium and Thorium standard in a different geometry. An aluminium can containing 2.147 g of Uranium standard,

2.202 g of Thorium standard and 5 g of epoxy glue in each can. The En value was also calculated for each standard as represented in Table 5 and Table 6.

Radionuclide	Reference value (Bq/g)	Uncertainty (Bq/g) k=2	Lab value (Bq/g)	Uncertainty (Bq/g) k=1	Expanded uncertainty at k=2 (Bq/g)	E_n value
Bi-214	4.939	0.025	4.881	0.104	0.208	**0.277**
Pb-214	4.939	0.025	4.977	0.184	0.368	**0.103**
Pb-210	4.939	0.025	4.539	0.682	1.364	**0.293**
Th-234	4.939	0.025	4.866	0.489	0.987	**0.075**

Table 5: En value calculation results for Uranium standard (aluminium can)

Radionuclide	Reference value (Bq/g)	Uncertainty (Bq/g) k=2	Lab value (Bq/g)	Uncertainty (Bq/g) k=1	Expanded uncertainty at k=2 (Bq/g)	E_n value
Ac-228	3.246	0.065	3.057	0.092	0.183	**0.969**
Pb-212	3.246	0.065	3.124	0.250	0.500	**0.242**
Tl-208	1.169	0.065	1.117	0.045	0.090	**0.464**
Ra-224	3.246	0.065	3.023	0.260	0.520	**0.426**

Table 6: En value calculation results for Thorium standard (aluminium can)

With the two geometries, it was discovered that Th-234 and Pb-210, applicability of LabSOCS was limited, because of their high uncertainty values.

The uncertainty of activity concentration of the Uranium standard in a metallic can as shown in Table 7 was compared using the standard and LabSOCS for efficiency calibration.

Isotope	Activity concentration using standard for efficiency calibration(Bq/g)	Activity concentration using LabSOCS for efficiency calibration (Bq/g)
Pb-210	4.672±0.112	4.661±1.402
Bi-214	4.866±0.029	4.874±0.210

Pb-214	4.941±0.022	5.046±0.352
Th-234	4.929±0.071	4.915±1.006

Table 7: Comparing uncertainty values using standard and LabSOCS efficiency calibration using metallic can

In respect to Table 7, using standard to calibrate the detector system gives less uncertainty as compared to LabSOCS especially for the low energy region.

4.3 ROBUSTNESS

Checking for robustness of the procedure is limited for this analysis procedure because:

1. User dependent effect was avoided because parameters selected for analysis were defined and were constant for all analyses. This was done by using the analysis sequence package in Genie 2000 software.
2. Efficiency stability was monitored by the quality assurance package.

Firstly, the robustness check of the method was carried out by using different variations of chemical composition to see the level of the sensitivity (to see if there could be any effect on the results) of knowing the exact composition. Since most samples analysed by the laboratory lack exact chemical composition, best estimates are usually assumed. Results from 4 different variations were compared using the hay sample and the Uranium standard. Isotopes checked with their respective gamma lines include Pb-210 (46.54 keV), Th-234 (63.29 keV), Pb-214 (242, 295.22 and 351.93 keV), Bi-214 (609.31, 1120.29 and 1764.29 keV), Cs-134 (604.70 and 801.93 keV), and Cs-137 (661.66 keV).

Density of RGU 1.4696 g/cm^3 was kept constant, and the same spectrum was used for the 4 readings. The analysis was done with the following chemical composition with mass ratios: Silicon (Si) - 46.40 %, Oxygen (O)- 53.41 %, Aluminium (Al)- 0.10 %, Calcium (Ca)- 0.02 %, Iron (Fe)- 0.03 %, Uranium (U)- 0.04 % - referred to Reading 1. The second analysis was composed of: Si- 50.90 %, O- 48.91 % - referred to Reading 2. The third analysis is made up of: Si- 39.31 %, O- 60.50 % - referred to Reading 3. The fourth analysis is made up of: Si- 5 %, O- 94.81 % - referred to Reading 4. Changes were done mostly with Silicon and Oxygen since the

other elements have very small quantities and therefore are insignificant. Results are presented in Table 8:

All uncertainties are presented at the 95 % confidence level.

Radionuclide	Reading 1			Reading 2			Reading 3			Reading 4		
	Lab value (Bq/g)	Uncertainty (Bq/g)	Bias (%)	Lab value (Bq/g)	Uncertainty (Bq/g)	Bias (%)	Lab value (Bq/g)	Uncertainty (Bq/g)	Bias (%)	Lab value (Bq/g)	Uncertainty (Bq/g)	Bias (%)
Pb-210	4.699	1.414	**4.68**	4.769	1.434	**3.44**	4.593	1.382	**7.01**	4.088	1.230	**17.23**
Th-234	4.915	0.986	**0.49**	4.944	0.992	**0.10**	4.871	0.978	**1.38**	4.657	0.936	**5.71**
Pb-214	5.035	0.352	**1.94**	5.053	0.352	**1.94**	5.035	0.352	**1.94**	5.047	0.354	**2.19**
Bi-214	4.592	0.198	**7.03**	4.593	0.197	**7.01**	4.593	0.197	**7.01**	4.981	0.214	**0.85**

Table 8: Variation of the chemical compositions of Uranium standard

The density of the hay sample 0.404 g/cm^3remained unchanged. The first analysis (cellulose) with a chemical composition of: $C_6H_{10}O_5$ - referred to Reading 1. The second analysis (lignin) with a chemical composition of: $C_{10}H_{12}O_3$ - referred to Reading 2, the third analysis (hemicellulose) with chemical composition of: $C_{31}H_{34}O_{11}$ - referred to Reading 3 and the fourth analysis (90 % cellulose + 10 % Potassium, Phosphorus and Calcium) with chemical composition of: $C_6H_{10}O_5$ - referred to reading 4. Results are presented in the Table 9 below.

Radionuclide	Reading 1			Reading 2			Reading 3			Reading 4		
	Lab value (Bq/g)	Uncertainty (Bq/g)	Bias (%)	Lab value (Bq/g)	Uncertainty (Bq/g)	Bias (%)	Lab value (Bq/g)	Uncertainty (Bq/g)	Bias (%)	Lab value (Bq/g)	Uncertainty (Bq/g)	Bias (%)
Cs-134	0.082	0.0083	**0.11**	0.082	0.0083	**0.11**	0.081	0.0083	**1.33**	0.082	0.00834	**0.11**
Cs-137	0.743	0.0864	**0.38**	0.74	0.0862	**0.38**	0.74	0.0862	**0.38**	0.74	0.0860	**0.38**

Table 9: Variation of the chemical compositions of hay

For this test, with results shown in Table 8, in comparing the bias of the exact composition with the other variations, it was seen that the bias varies more in the low energy region as compared to the high energy region. And for Table 8 and Table 9, we can see that the deviation between results and reference value is below 20 %. But we do not have best conditions to have a

satisfactory result; we can expect more complications in real life situations when the exact composition may not be known for complicated samples.

A graphical robustness check was done in terms of the efficiency calibration used for each analysis made in Table 3 and Table 4 as shown in Figure 19 and Figure 20.

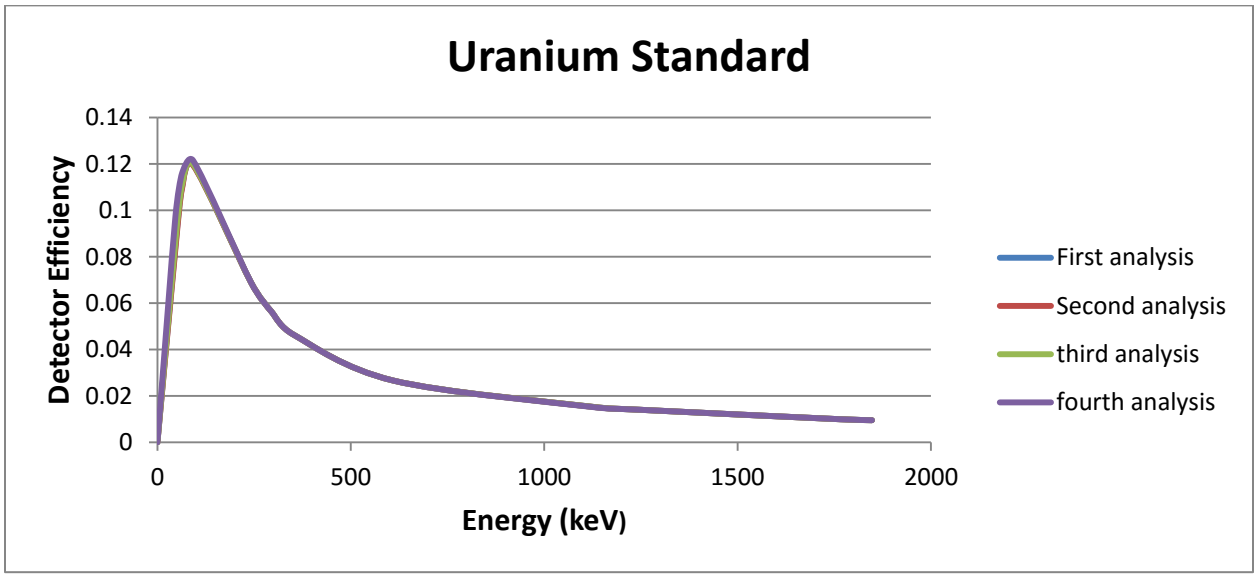

Figure 19: Checking for robustness to see the difference in efficiency calibration by changing the chemical composition of samples in uranium standard

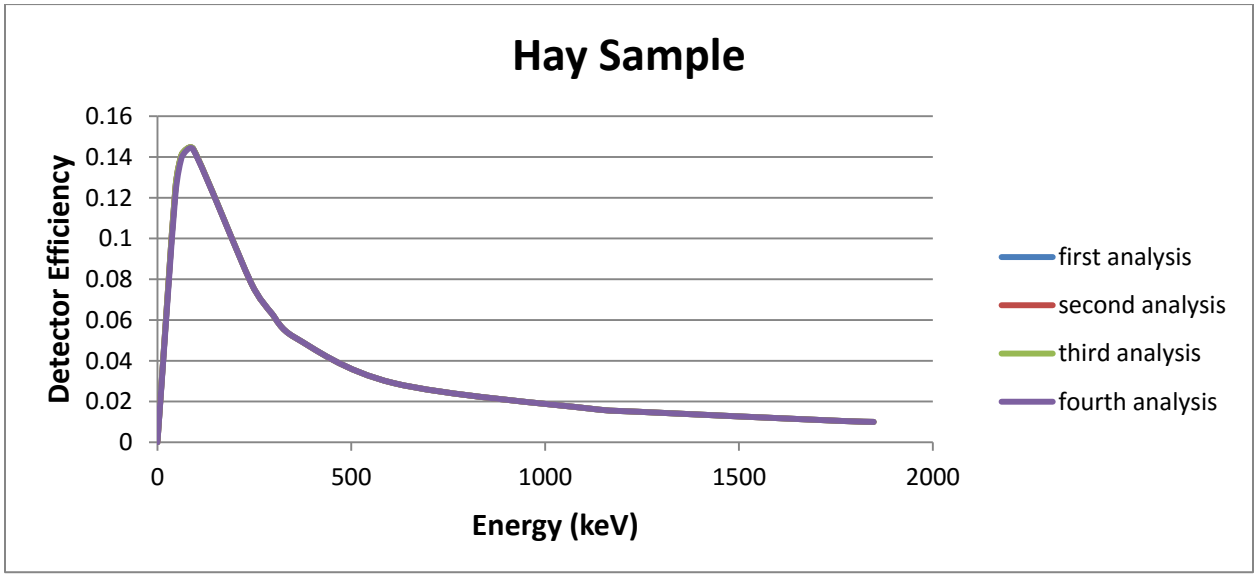

Figure 20: Checking for robustness to see the difference in efficiency calibration by changing the chemical composition of samples calibration in hay sample

The test observations show that the analysis procedure is robust as the variation of the chemical composition has no significant effect on the detector efficiency, as shown in Figure 19 and Figure 20.

4.4 PRECISION

4.4.1 Quality Assurance

Firstly, the Thorium standard was used to check the variability of the following radionuclides Ac-228, and Pb-212, and the Uranium standard for Pb-214. Seven parallel measurements between January 2015 and March 2016 were used to check the precision of the analysis procedure in terms of activity concentration reports of the standards are shown in the quality assurance charts in Figure 21- Figure 23.

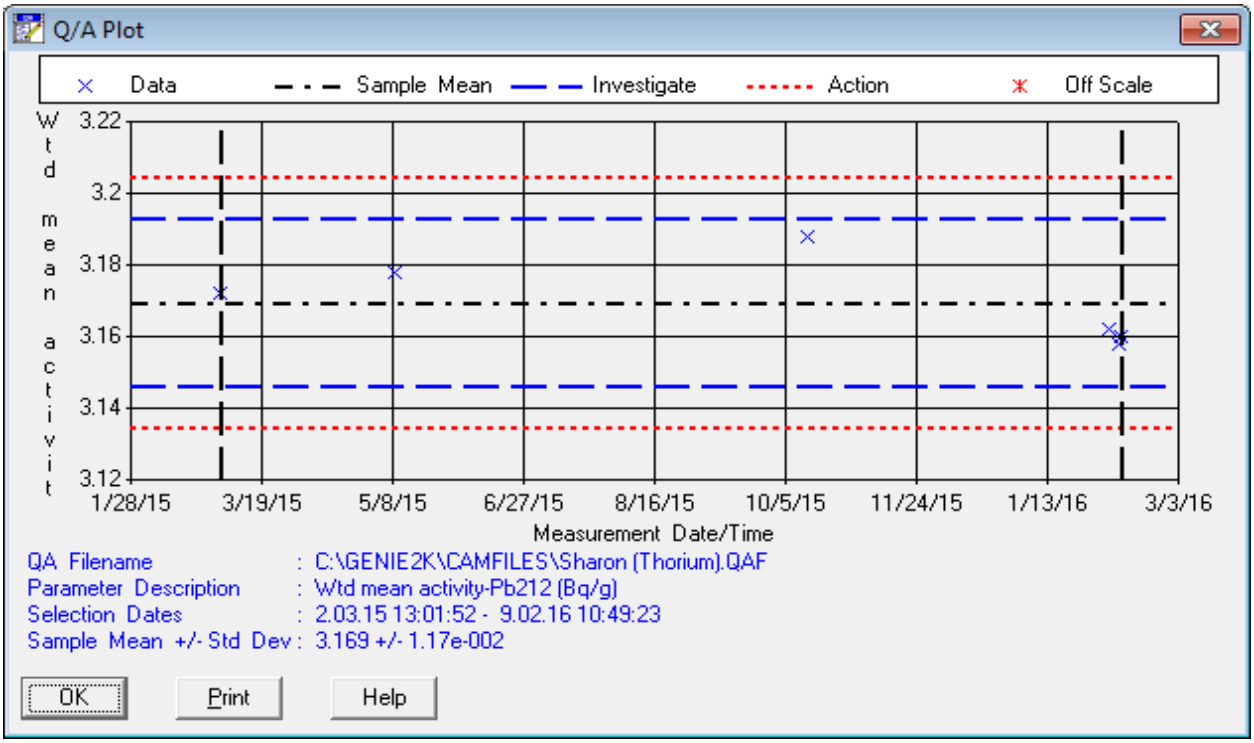

Figure 21: Quality Assurance chart of Thorium standard for Pb-212

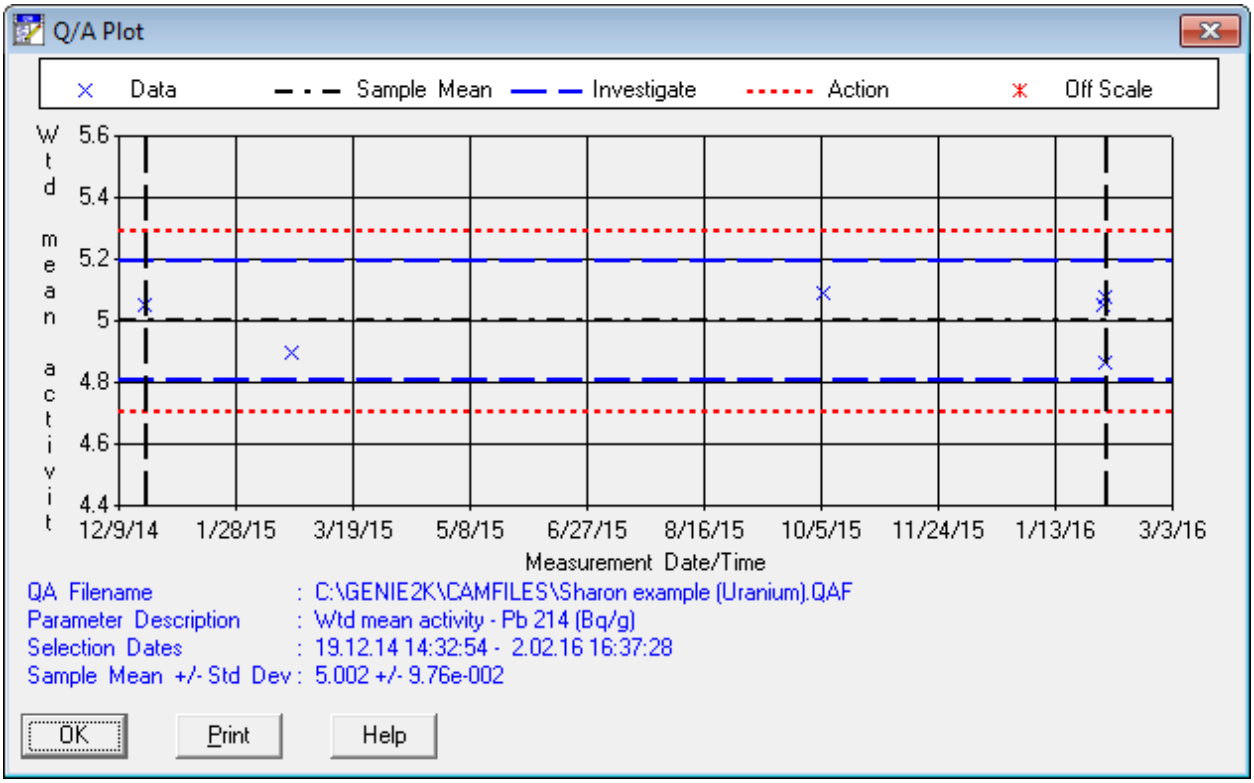

Figure 22: Quality Assurance chart of Uranium standard for Pb-214

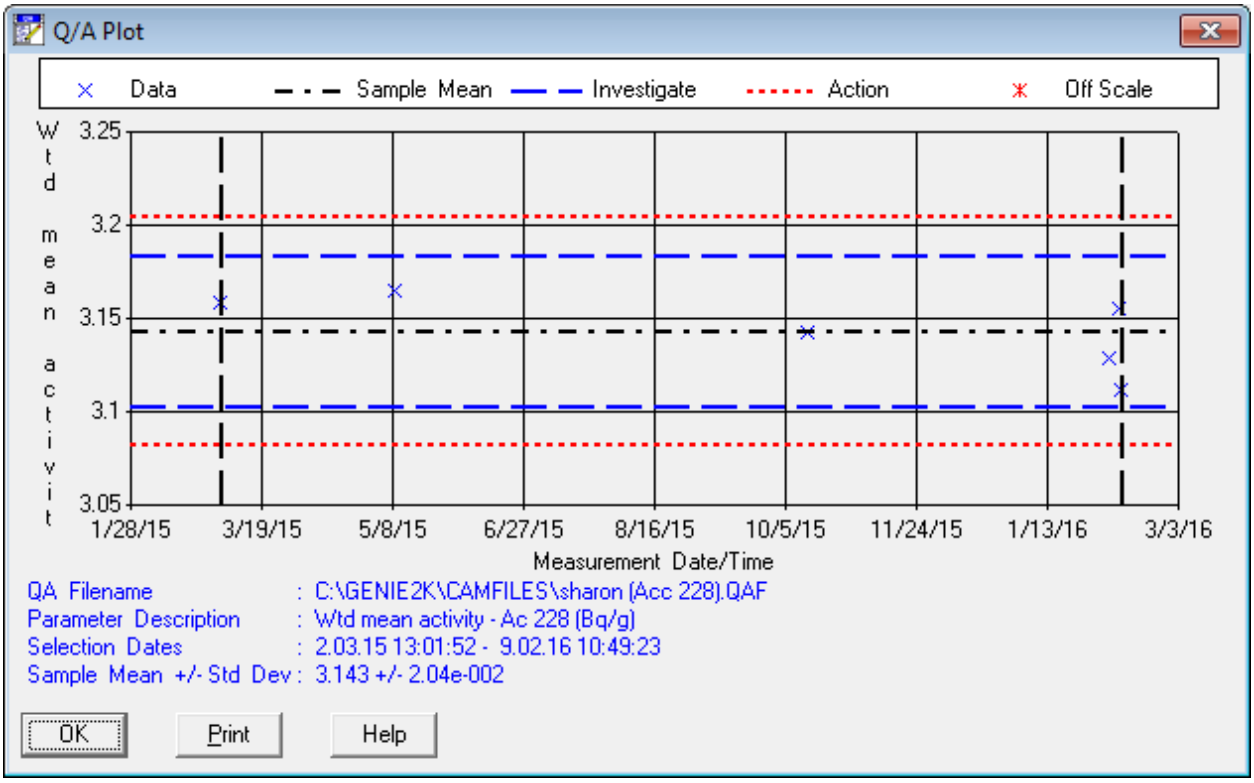

Figure 23: Quality Assurance Chart of Thorium standard for Acc-228

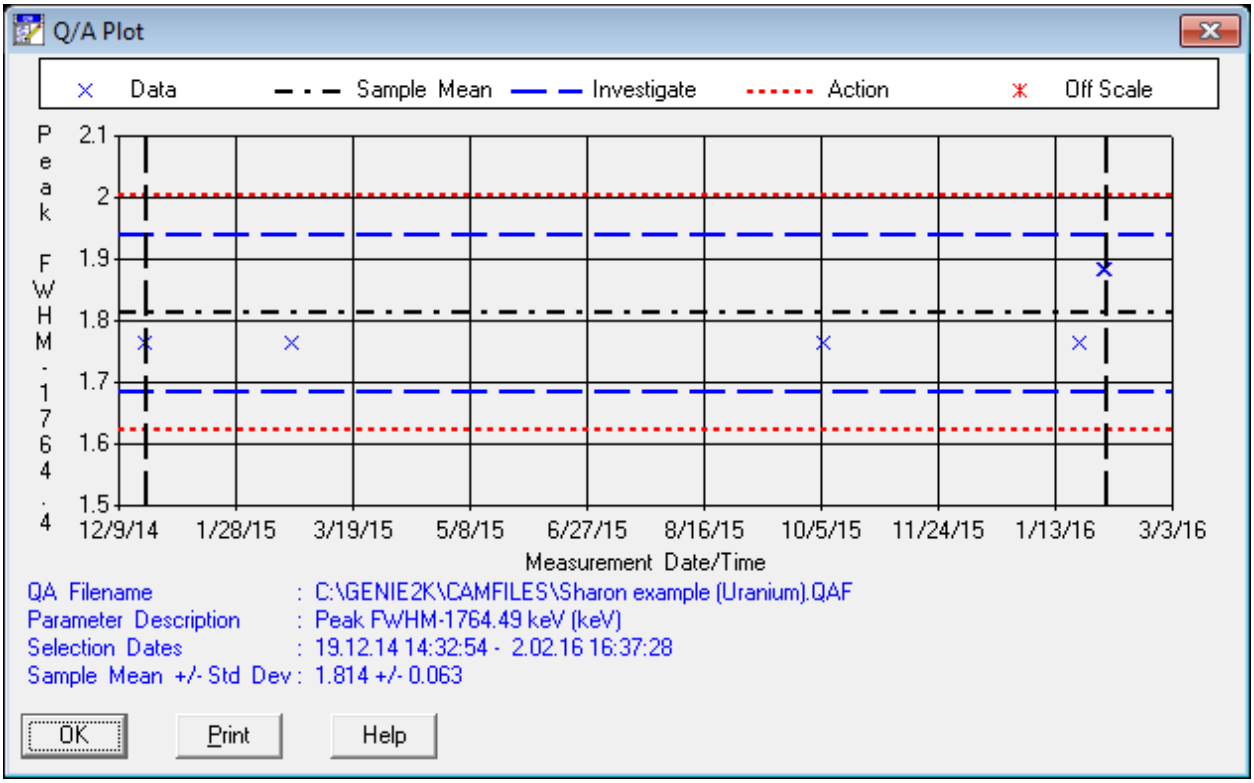

Figure 24: Quality Assurance chart for Uranium Standard for Bi-214

The full width at half maximum was used to monitor Bi-214 at energy 1764.49 keV as shown in Figure 24 to monitor the peak width as the FWHM also affects how the precise analysis procedure is.

The results on the standards shown above with horizontal lines indicate the accepted limit (black, dot-and-dash lines) means $\pm 1\sigma$. Warning line (blue, long dashed lines) mean $\pm 2\sigma$and action line (red, dotted lines) mean $\pm 3\sigma$ respectively as explained in Chapter 3. From the quality assurance chart, it was seen that the activity concentration results fell within the acceptance limit. And overtime, the results will be monitored, and if needed, corrective action will be made, if the results differ from the acceptable range.

The, precision was also expressed in terms of relative standard deviation (RSD) as shown in Table 10 and Table 11:

Isotope	Activity after decay (Bq/g)	Lab value (Bq/g)			RSD (%)	Pooled uncertainty (%)
		Reading 1	Reading 2	Reading 3		
Ac-228	3.246±0.065	3.128±0.242	3.347±0.199	3.159±0.188	**3.69**	**3.38**
Pb-212	3.246±0.065	3.161±0.512	3.158±0.512	3.160±0.512	**0.05**	**8.10**
Tl-208	1.169±0.065	1.058±0.084	1.061±0.083	1.056±0.084	**1.45**	**3.91**
Ra-224	3.246±0.065	3.020±0.508	3.023±0.510	2.999±0.508	**0.43**	**8.44**

Table 10: Relative standard deviation of Thorium standard

Isotope	Activity after decay (Bq/g)	Lab value (Bq/g)			RSD (%)	Pooled uncertainty
		Reading 1	Reading 2	Reading 3		
K-40	13.573±0.091	13.834±1.126	13.918±1.140	13.823±1.126	**0.37**	**4.08**

Table 11: Relative standard deviation of Potassium standard

Generally, it was observed from the tests performed that the RSD results are fewer than 5 %, showing that the precision of this method was considered to be very good. The RSD was then also compared with the pooled standard uncertainty. The pooled standard uncertainty was found to be higher than the RSD, which is good; as this shows that all uncertainty contributions are taken into account. But still the pooled standard uncertainty is considerably high, which means uncertainty is overestimated for Pb-212 and Ra-224.

Secondly, testing for precision was done by checking the variations in background spectra; specific peaks with gamma lines 45.6 (Pb-210), 186.6 (Ra-226), 238.3 (Pb-212), 352 (Pb-214), 1460.5 (K-40) keV respectively were checked to compare over time, from November 2014 until February 2016. Measurement time varied during this period. These peaks were checked to monitor the stability of the background spectra and also check if they are properly subtracted in the sample spectrum. This test was to know how precise the analysis procedure was, background measurement was important to check for some factors that will affect efficiency of measurement over a period of time; and therefore the need to check for background variations.

Repeatability calculations for the background spectra were compared for standard deviations of the net peak area, and the pooled standard uncertainty for seven background spectra using Equation 21. Results are presented in Table 12:

$$s_{pooled} = \sqrt{\frac{{s_1}^2+{s_2}^2+{s_3}^2+\cdots{s_k}^2}{k}} \quad [21]$$

Where,

k is the number days of measurements

s_1, s_2 are the group standard deviations.

Background	Peak engergy (kEV)	Total peak area	Uncertainty k=1	Net peak area (counts/sec)	Relative uncertainty	Relative Standard deviation (net peak area)	Pooled standard uncertainty
1	**46.6 Pb-210**	673	37	0.0029	0.0547	**0.0432**	**0.05148**
2		581	33	0.0032	0.0576		
3		472	31	0.0029	0.0664		
4		1040	45	0.0031	0.0430		
5		833	40	0.0031	0.0482		
6		1380	51	0.0032	0.0373		
7		847	40	0.0032	0.0476		
1	**186.6 Ra-226**	770	46	0.0033	0.0594	**0.0505**	**0.0608**
2		542	40	0.0030	0.0741		
3		532	39	0.0033	0.0726		
4		1040	54	0.0031	0.0522		
5		902	50	0.0034	0.0553		
6		1300	62	0.0030	0.0476		
7		802	48	0.0030	0.0597		
1	**238.3 Pb-212**	460	40	0.0020	0.0862	**0.0910**	**0.0944**
2		304	34	0.0017	0.1133		
3		308	33	0.0018	0.1085		
4		595	47	0.0018	0.0792		
5		472	42	0.0018	0.0888		
6		704	53	0.0016	0.0749		
7		402	41	0.0015	0.1028		
1	**352 Pb-214**	241	30	0.0010	0.1264	**0.1992**	**0.1142**
2		212	27	0.0011	0.1293		
3		232	28	0.0014	0.1204		
4		448	38	0.0013	0.0852		
5		399	35	0.0015	0.0877		
6		400	41	0.0009	0.1035		
7		240	33	0.0009	0.1357		
1	**1460**	147	15	0.0006	0.1008	**0.1710**	**0.0895**

2	**K-40**	112	13	0.0006	0.1170		
3		148	14	0.0009	0.0955		
4		266	19	0.0008	0.0717		
5		243	18	0.0009	0.0744		
6		268	20	0.0006	0.0751		
7		207	17	0.0008	0.0823		

Table 12: Table of background spectrum data

The pooled combined uncertainty was expected to be higher than the relative standard deviation, and in this way we know that the uncertainty is not underestimated.

From the raw data in Table 12, the statement above was justified, Pb-210 for the relative standard deviation and pooled standard uncertainty are comparable with 4.3 % and 5.1 % respectively, meaning that the Lead content in the environment is correctly estimated for this period of time. The same assumption can be made for Ra-226 and Pb-212 which has comparable results. Except for Pb-214 with 20 % and 11 %, K-40 with 17 % and 9 % for relative standard deviation and pooled standard uncertainty where uncertainties are underestimated. These could be as a result of high count rate of K-40 and lots of Potassium in the environment, and the state of the environmental condition at the particular period when the measurement was taken.

4.5 DETECTION LIMIT

The limit of detection values depends on the nuclide content of a sample, which means these values presented below can vary, because it does not depend only on the detection system and measurement conditions (18).

These variations depend significantly on the detector-sample geometry, the sample quantity, and the shape, the detector type (size), the background level of the detection system, the composition of radionuclides in the sample, and the measurement time period.

According to the experiments carried out, the analysis procedure can determine all gamma-rays emitting radionuclides which are calibrated in the energy range (18). The MDA provided for a Uranium standard dependent on the following: detector-sample geometry distance of 4.50 cm, mass of 83.7677 g in a metallic can, with the chemical composition Silicon (Si) - 46.40 %, Oxygen (O)- 53.41 %, Aluminium (Al)- 0.10 %, Calcium (Ca)- 0.02 %, Iron (Fe)- 0.03 %,

Uranium (U)- 0.04 %, with n-type 71 mm planar Canberra detector, sample count time of 69581.560 seconds, and background measurement count time of 264191.400 seconds.

The minimum detectable activity (MDA) can range as follows:

MDA (Th-234) - 0.0342 Bq/g

MDA (Pb-214) - 0.00611 Bq/g

MDA (Ra-226) - 0.0418 Bq/g

MDA (Bi-214) - 0.00511 Bq/g

MDA (Pb-210) - 0.0597 Bq/g

4.6 UNCERTAINTY BUDGET

4.6.1 LabSOCS Uncertainty Estimation

The correction term estimated in the previous section introduces an uncertainty, and since the efficiency values are constant for a particular geometry, an uncertainty factor was estimated for the low and high energy region as seen in Figure 10 where there is always a cross over between those energies. A calibration curve was built using the standard sample and compared with a calculated efficiency using the peak to peak efficiency formulae as shown in Equation 22:

$$E_{pp} = \frac{S}{V \times y \times T_1} \quad [22]$$

Where all symbols remain the same as Equation 4. Table 13 below summarizes the results using the Uranium standard.

Energy (keV)	Efficiency	Intensity (%)	Live time (secs)	Mass (g)	net peak area	Activity standard (Bq/g)	Peak to Peak efficiency	deviation
46.54	0.0744	4.25	69581.56	83.7677	86400	4.939	0.0706	0.0511
63.29	0.1172	3.77			127000		0.1170	0.0018
92.6	0.1773	4.33			221000		0.1773	0.00002
242	0.0906	7.27			189000		0.0903	0.0036
295.22	0.0759	18.41			402000		0.0759	0.0009
351.98	0.0648	35.60			663000		0.0647	0.0009
609.31	0.0314	45.49			411000		0.0314	0.0011
1120.29	0.0185	14.91			79200		0.0185	0.0015
1238.11	0.0170	5.83			28400		0.0169	0.0023
1764.49	0.0151	15.31			66300		0.0150	0.0011

Table 13: Deviation between standard efficiency and calculated efficiency

Therefore, the mean of the deviation in low energy is 1.8 % and for the high energy is 0.16 % at k=1 confidence level. The split of the low and high energy was at 92.6 keV and this was because the 92.6 peak is not really a peak of interest compared to using other peaks as the crossover. This uncertainty value has to be included in the uncertainty budget.

4.6.2 Uncertainty budget

Using Equation 8, an uncertainty budget illustrated in Table 14 was made for activity concentration Pb-214 with gamma line 351.9 keV. These values are different for each gamma line. Quantities are explained in Equation 7.

Quantity	Value	Uncertainty component	Uncertainty component	Relative Standard uncertainty	Distribution	Index (%)
Efficiency ($\sigma_{\varepsilon'}$)	0.0465	0.00279		0.0600		**99.83**
Net peak area (σ_S)	663000	824		0.0012	normal	**0.04**
Volume (σ_V)	83.7677 g	0.0011		0.0000137	normal	**0.00**
Intensity (σ_y)	49.83 %	0.140	0.16	0.0021	normal	**0.13**
Live time	69581.56 seconds	0		0		**0.00**
Coincidence summing(σ_K)	1					
A	4.909 Bq/g			$\sigma_c = 0.295$ Bq/g		

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
Activity concentration (A)	**4.909 Bq/g**	**0.590 Bq/g**	2.00	95 % normal

Table 14: Uncertainty budget

There was no readily available information about uncertainty of live time and that was why it was considered zero.

5 CONCLUSION AND OUTLOOK

The aim of this work was to develop and validate a measurement procedure that measures all gamma-ray emitting radionuclides by gamma spectrometry. The validation parameters that were investigated were accuracy, robustness, detection limit and precision. The tools used for validation were the validated modelling tools (EFFTRAN) and certified reference materials.

During the validation of the analysis procedure, it was clear that LabSOCS software as a calibration tool was not calibrated for the laboratory specific detector. This failure on the part of the supplier brought into question the accuracy of the LabSOCS analysis procedure. This was discussed with the supplier, and they confirmed our findings were correct and action has been taken on it. If action goes well, we can get rid of the correction factor and the uncertainty associated with it, even though negligible. Nevertheless, the measurement system is without failure, it is operational but there are limitations.

From the validation process, it was shown that:

- The analysis procedure meets requirement for robustness considering that the results were on a satisfactory level when compared with certified reference materials. There was no significant change in efficiency curve with variation in chemical composition.
- The analysis procedure can produce reliable, highly satisfying and accurate results with the investigation carried out so far with high energy range radionuclides. In terms of accuracy, all standardised errors were found to be under the maximum value of 1 but total uncertainty for low energy region Pb-210 and Th-234 were above 20 %.
- The procedure has good repeatability in terms of background measurement for Pb-210, Ra-226, and Pb-212. For Pb-214 and K-40 showed fluctuation overtime. This can be as a result of variation in gamma radiation when the measurement was made. To check the variation of these two radionuclides when the spectrum is obtained, a routine quality assurance check should be done every 4 months to monitor the background spectra.
- The procedure has good repeatability in sample measurement, which was confirmed by checking the activity concentrations measured for some set of radionuclides using the quality assurance package within the Genie analysis software, this also has to be monitored over time.
- To avoid that level of uncertainty from the efficiency, precise geometric characterisations should be done for the laboratory specific detector; this will increase the accuracy of the analysis

procedure. To improve the accuracy of LabSOCS, it is also recommended to perform calibration using standard where LabSOCS accuracy is a question as explained in Table 7.

In conclusion, the validation parameters show that the analysis procedure is fit for high energy range radionuclides as the design of the system is limited but not a failure.

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7 KOKKUVÕTE

Gammaspektromeetrilise analüüsiprotseduuri väljatöötamine ning valideerimine ülipuhta Germaaniumdetektoriga.

Oluwamayowa Sharon Sanni

Magistritöö õppekavas Rakenduslik mõõteteadus

Käesoleva uurimustöö eesmärk oli välja töötada ning valideerida gammaspektromeetriline analüüsiprotseduur, kasutades selleks ülipuhast germaaniumidetektorit.

Uue, kasutusele võetud, riistavara juurde kuuluv tarkvara LabSOCS (ingl. k. Laboratory Sourcless Calibration Software) võimaldab muuhulgas kalibratsiooni mõõtmisi teostada standardallikavabalt. LabSOCS põhineb detektori geomeetrilisel karakteriseerimisel, mis võimaldab omakorda korrektset süsteemi efektiivsuse kalibratsiooni.

Läbi viidud katsete käigus selgus, et laboris kasutusel olev detektor ei vasta kehtestatud protseduuristandarditele ning varustaja? oli geomeetrilise karakteriseerimise läbi viinud ebakorrektselt. Puuduse kõrvaldamiseks on käesolevas töös välja toodud võimalused? tulemuste täpsuse suurendamiseks.

Käesolevas magistritöös on kirjeldatud germaaniumdetektori mõõtetulemuste parandamiseks vajalikult parandusfaktorid ning nende rakendamise võimalused ja ka see, kuidas analüüsi protseduuri adresseeritud valideerimisparameetrite kasutades mitu sertifitseeritud teatmematerjalid.
Kirjeldatud parandusfaktoriteks olid mõõtetäpsus, kordustäpsus, avastamispiir ning robustsus. Saadud tulemused näitasid, et käsitletud analüüsiprotseduur on sobiv standardallikavaba mõõtmiste läbiviimiseks, kuna mõõdetud radionukliidide eriaktiivsuse kontsentratsioonid olid valdavalt vastavuses referentsmaterjali väärtustega.

Infoleht / Information sheet

Estonian

Gammaspektromeetrilise analüüsiprotseduuri väljatöötamine ning valideerimine ülipuhta Germaaniumdetektoriga.

Gammaspektromeetrilise analüüsiprotseduuri välja arendamiseks kasutati lai energia ülipuhast germaaniumdetektorit koos tarkvaraga Genie 2000. Antud tarkvara sisaldas riistprogrammi LabSOCS, mis võimaldab läbi viia standardivabu mõõtmisi. Eesmärgiga välja selgitada, kas käsitletud analüüsiprotseduur on sobiv standardallikavaba mõõtmisi teostada, viidi käesoleva magistritöö raames läbi ka analüüsiprotseduuri valideerimine.

Märksõnad: *LabSOCS, gammaspektromeetria, analüüsiprotseduur, ülipuhas Germaaniumdetektor, geomeetiline karakteriseerimine, valideerimine*

English

Development and validation of gamma spectrometric analysis procedure using a high purity Germanium detector.

A new detection system, broad energy high purity germanium detector with software (Genie 2000 software) was used to develop a gamma spectrometric analysis procedure. LabSOCS as a tool in Genie was needed to perform a standard-free calibration measurement. Validation of analysis procedure was important to know if the procedure is fit for purpose.

Keywords: *LabSOCS, gamma spectrometric, Analysis procedure, High purity germanium detector, Geometric characterisation, Validation*

CERCS code: P220

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